I^3N Innovative Integrated Instrumentation for Nanoscience

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High Resolution Electronic Measurements in Nano-Bio Science

Electrical measurements in liquids

Basic considerations

Giorgio Ferrari

Milano, June 2025

Outline

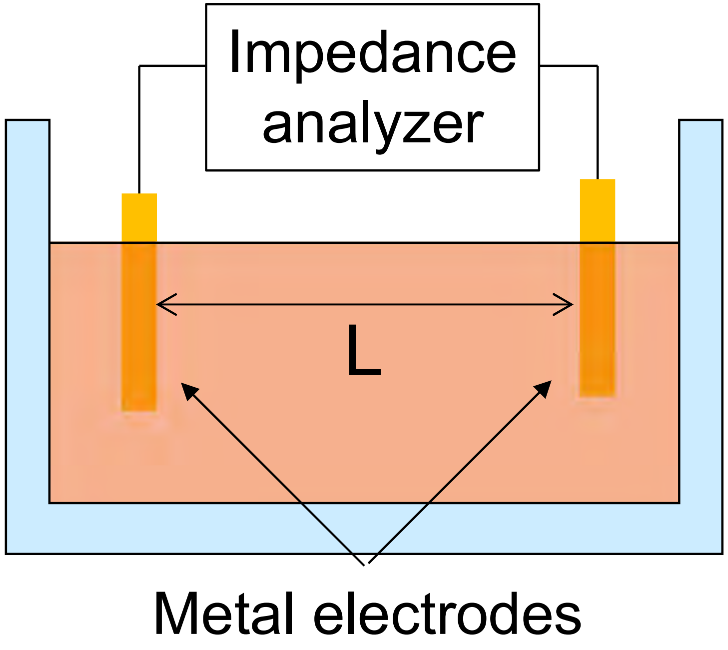
- Example of electrical measurements in liquid
- The electrical behavior of the (bulk) liquid
- Metal – liquid interface: charge redistribution
  - Double-layer capacitance

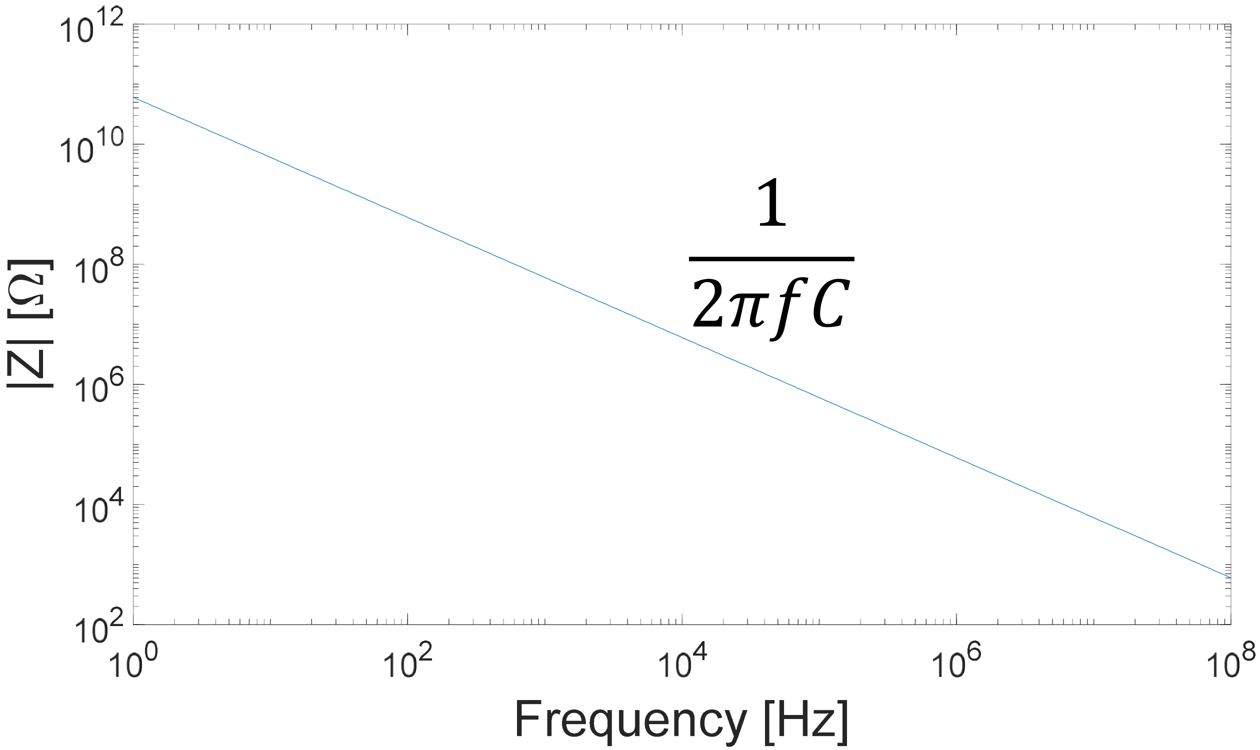
Next lessons:

- Charge transfer at the metal-liquid interface
- The importance of mass transport

Example 1

Oil





Parallel plate electrodes

A_{el}= 1cm x 1cm

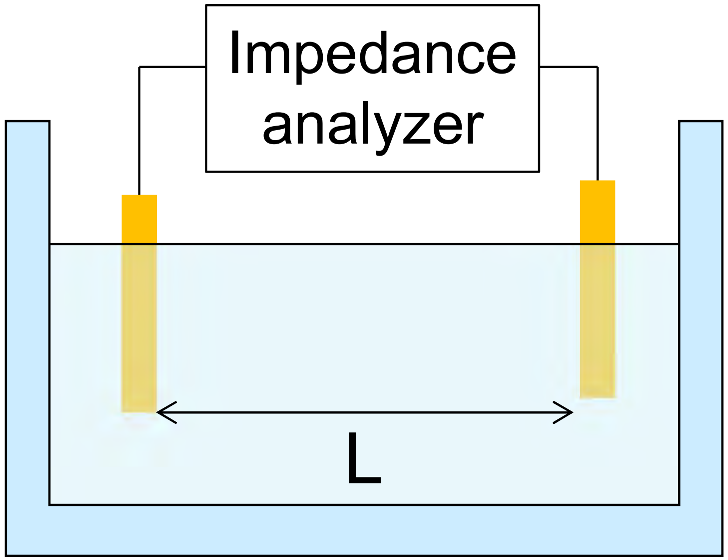
L= 1mm

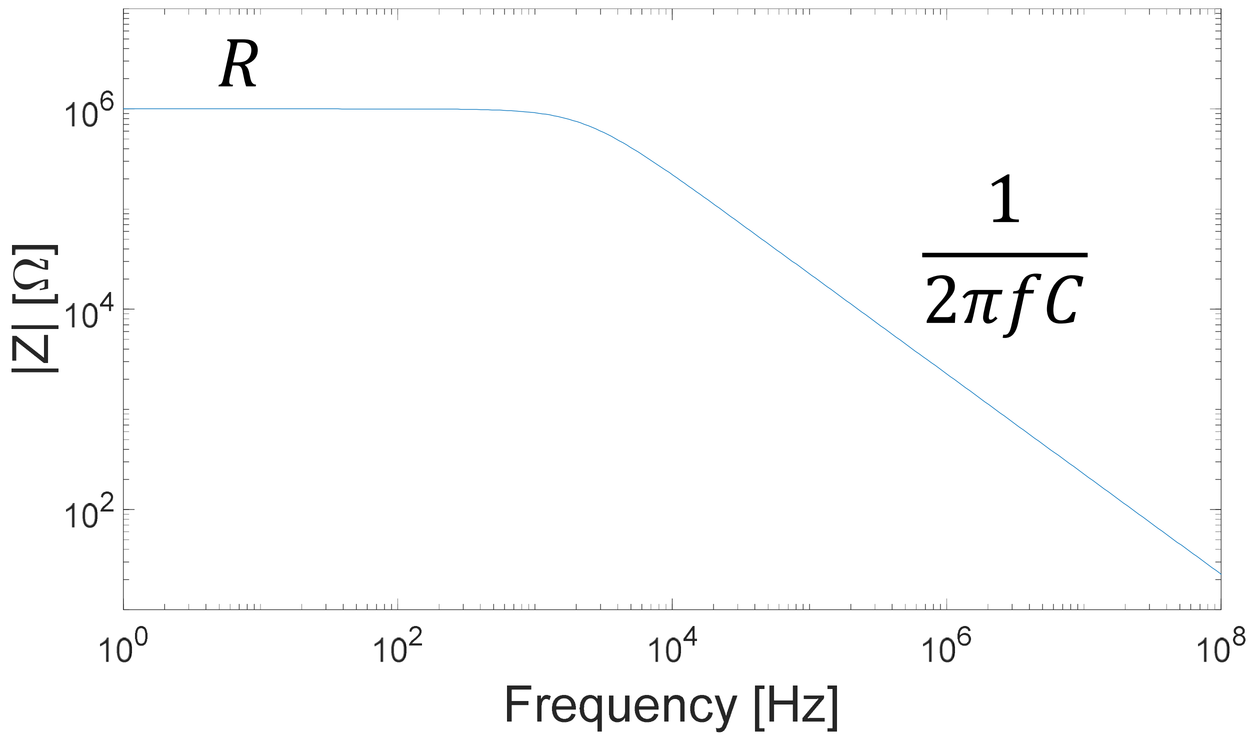
- Capacitive behavior $Z(f) = \frac{1}{j2\pi f\, C}$

$$C = \epsilon_r \epsilon_0 \, \frac{A_{el}}{L}$$

Example 2

Distilled water



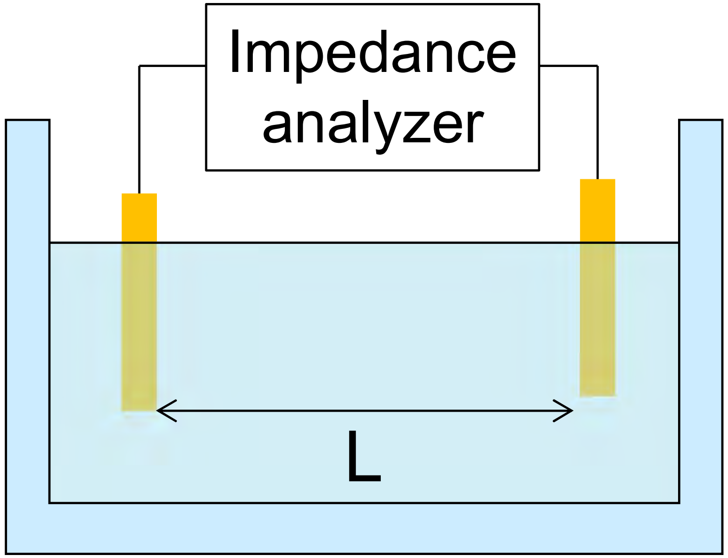


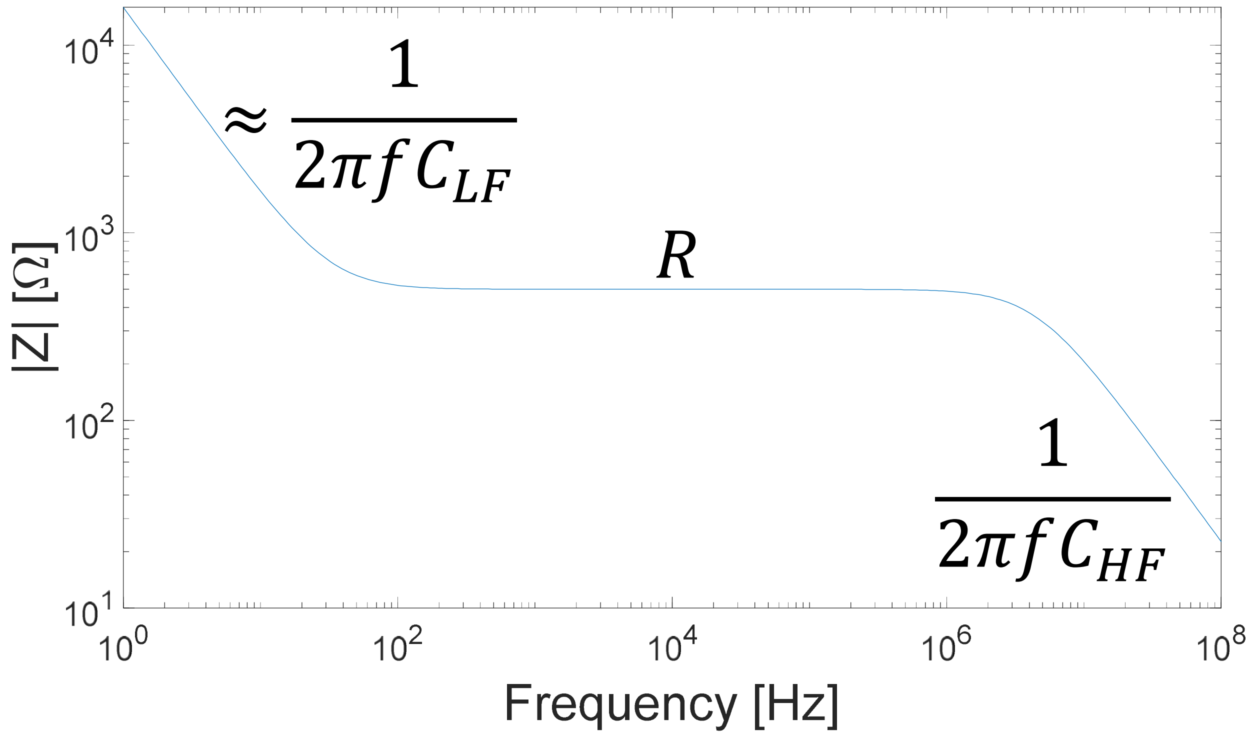
Parallel plate electrodes
A_{el}= 1cm x 1cm
L= 1mm

- Low frequency: resistive behavior
- High frequency: capacitive behavior

Example 3

Tap water



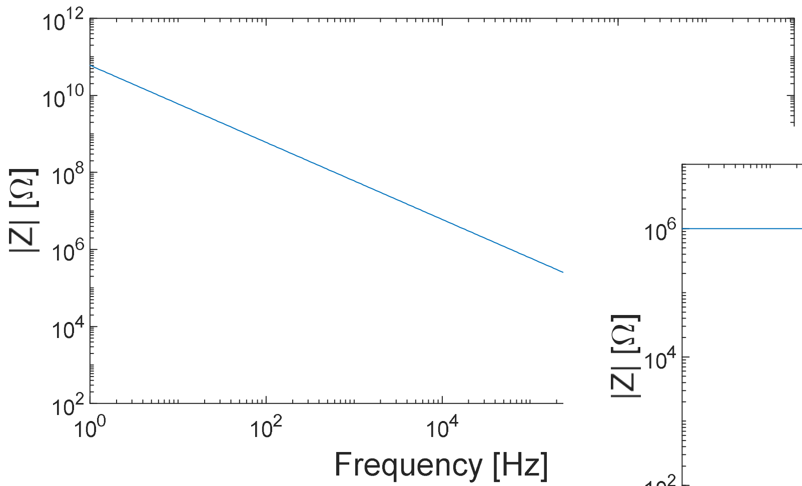


Parallel plate electrodes
A_{el}= 1cm x 1cm
L= 1mm

- Low frequency: ≈capacitive behavior
- Medium frequency: resistive behavior
- High frequency: capacitive behavior

The role of the ions

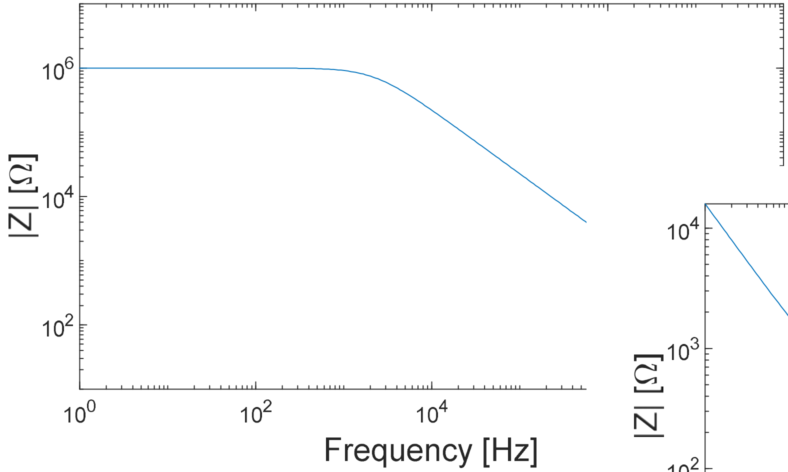
Oil



No ions

Dielectric behavior

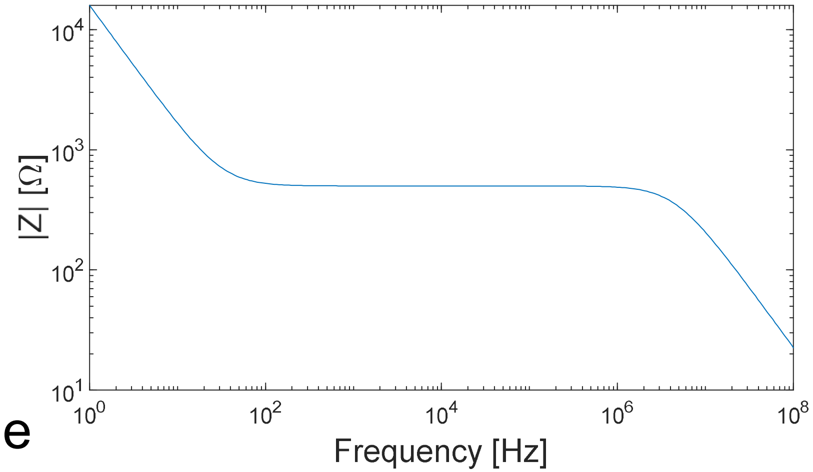
Distilled water



Few ions

Water is a polar molecule
→ high ϵ_r (≈ 80)

Tap water



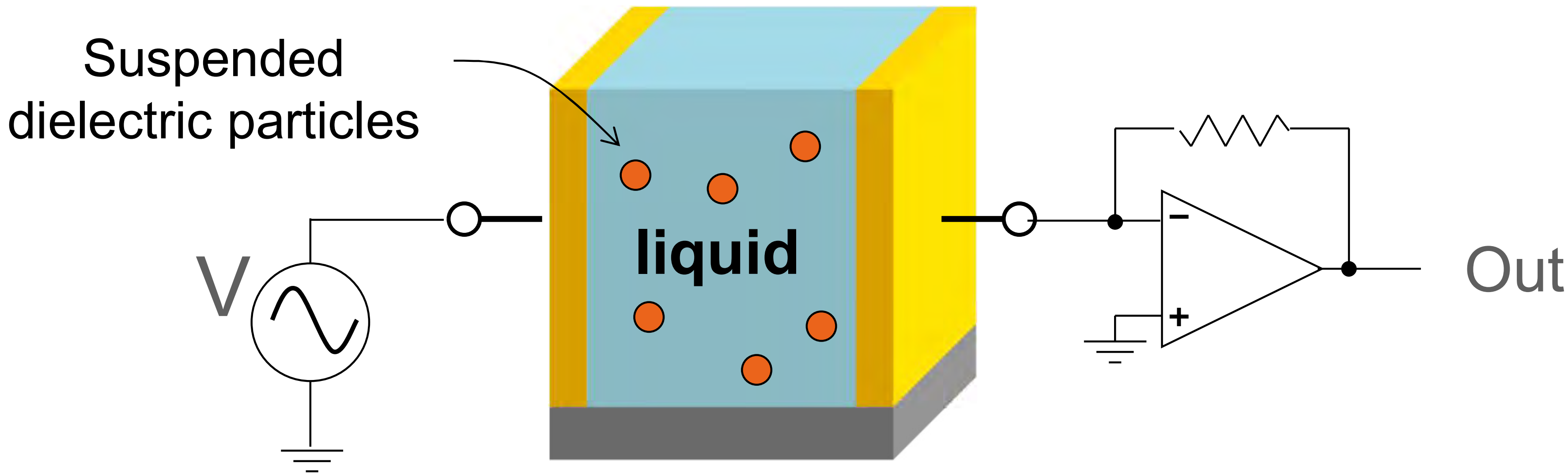
Many ions

The difference is given by the concentration of charge carriers

- Ions
- Charged particles

Example of electrical meas. of nonionic liquids

Analysis of suspended particles



$C_{liquid\ only} = \varepsilon_l \cdot S$ ε_l dielectric constant of the liquid, S geometrical factor

$C_{liquid+particles} = \varepsilon_e \cdot S$ → $\varepsilon_e = \varepsilon_l\, C_{liquid+particles} / C_{liquid\ only}$

For small particles (<10μm, effective medium theory):

$$f\,\frac{\epsilon_p - \epsilon_e}{\epsilon_p + 2\epsilon_e} = (1-f)\,\frac{\epsilon_l - \epsilon_e}{\epsilon_l + 2\epsilon_e}$$

f= volume fraction

ε_p dielectric const. of particles

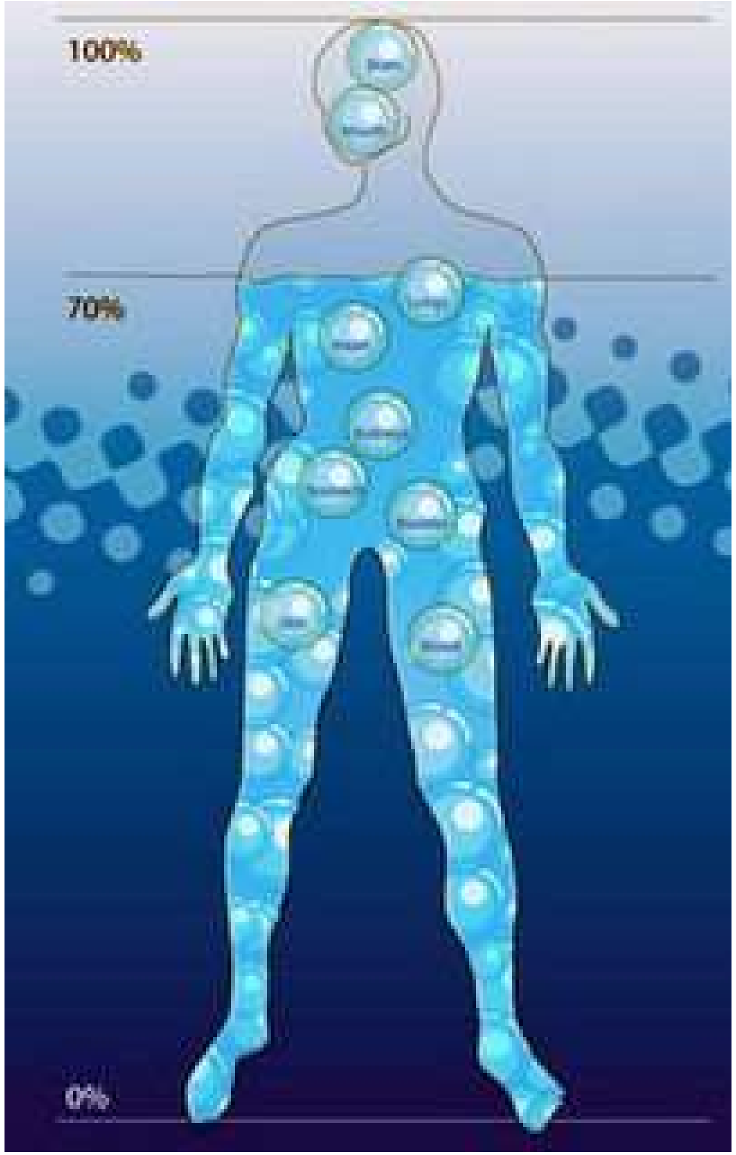
- 1925 (Fricke, Morse): cell membrane thickness (4nm!)
- dipole moment of molecules

[Thompson, J. Chem. Educ., 1966]

Electrical meas. of biological samples

- ~65% of body mass is water
- Cells, enzymes, proteins,…
  … "survive" only in water
  + a lot of ions

Biomedical devices
Biosensors
Bioelectronics interfaces
Bio+ …

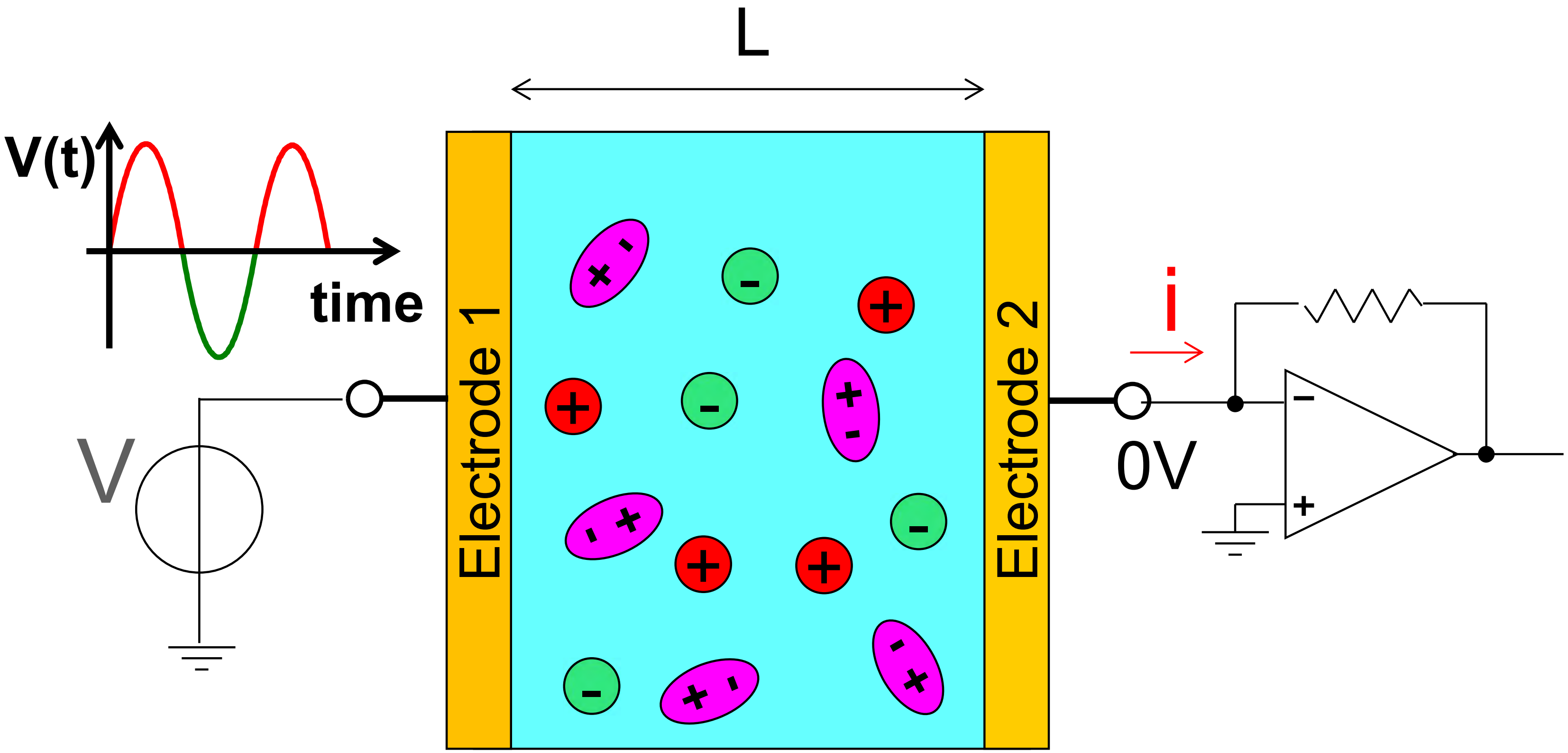


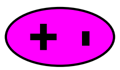
http://kangen.net/h2o-research/water-is-vital-to-life/

…must operate with ionic solutions (electrolytes)!

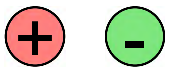
Electrolytes

Liquid (water)+ ions





Polar molecule (water)



Ions

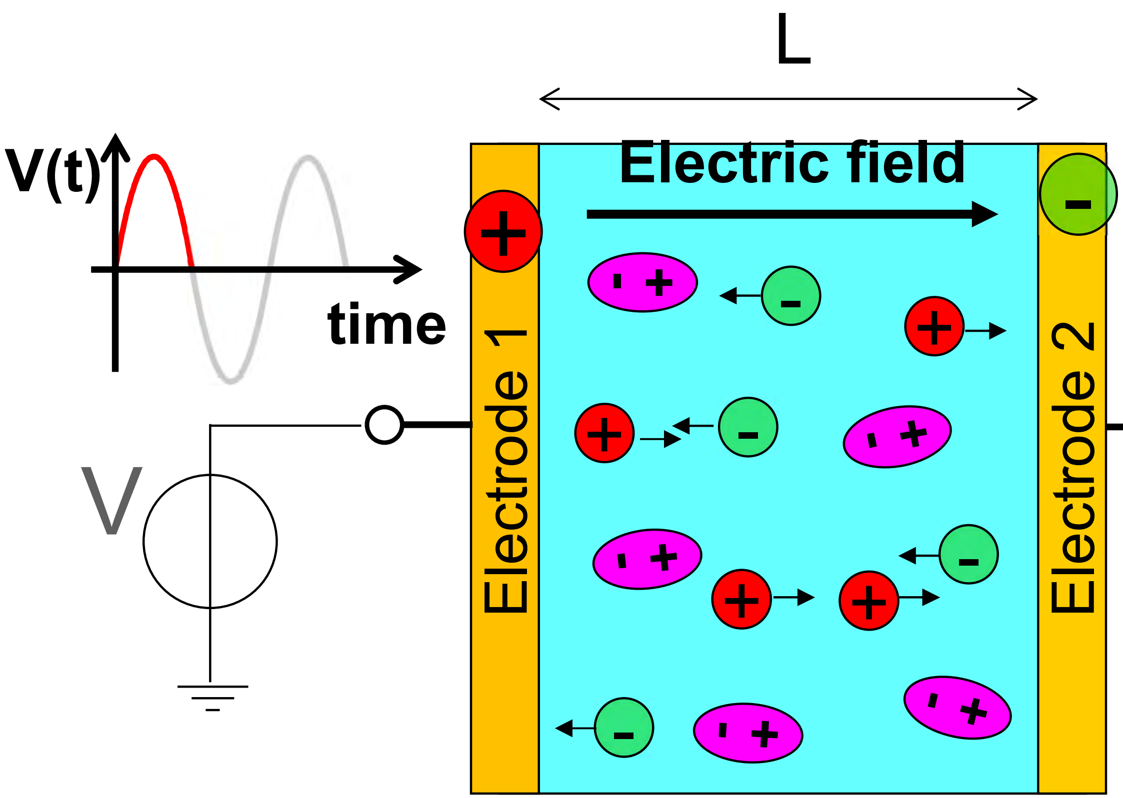
Electrolytes

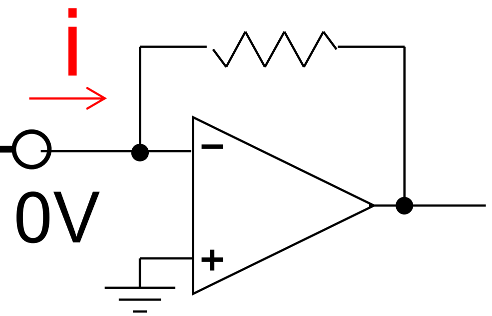
Liquid + ions

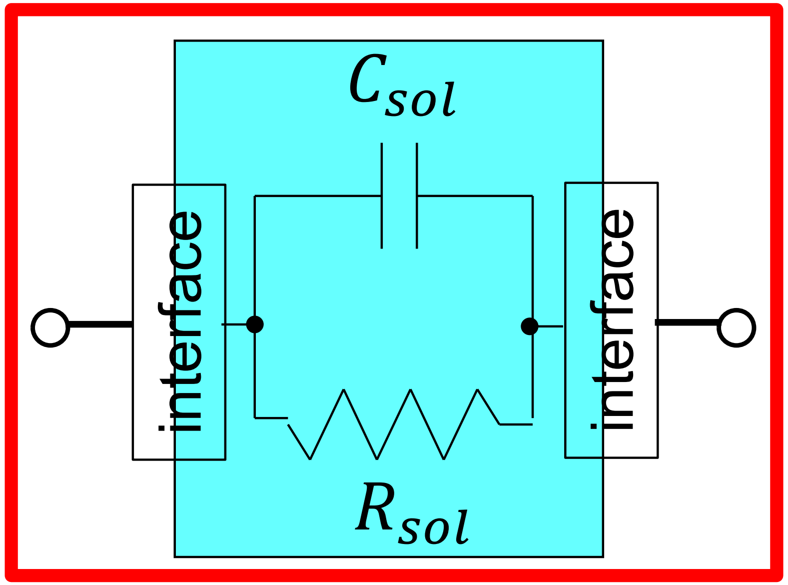
Conductive behavior

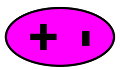
charge transport

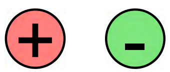
Current given by induced charge + transferred charge







 Polar molecule (water)

 Ions

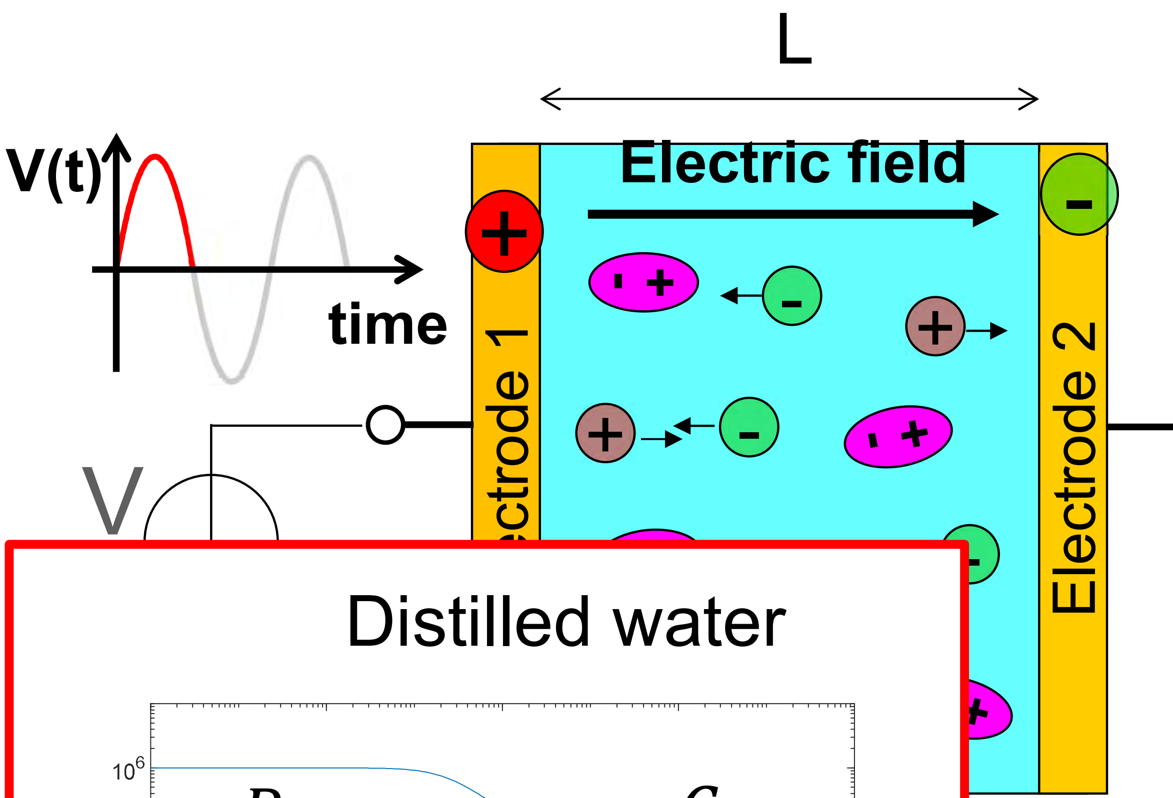
Electrolytes

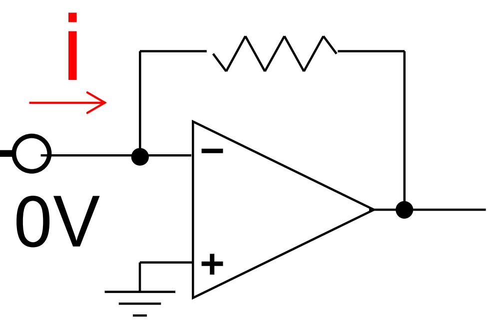
Liquid + ions

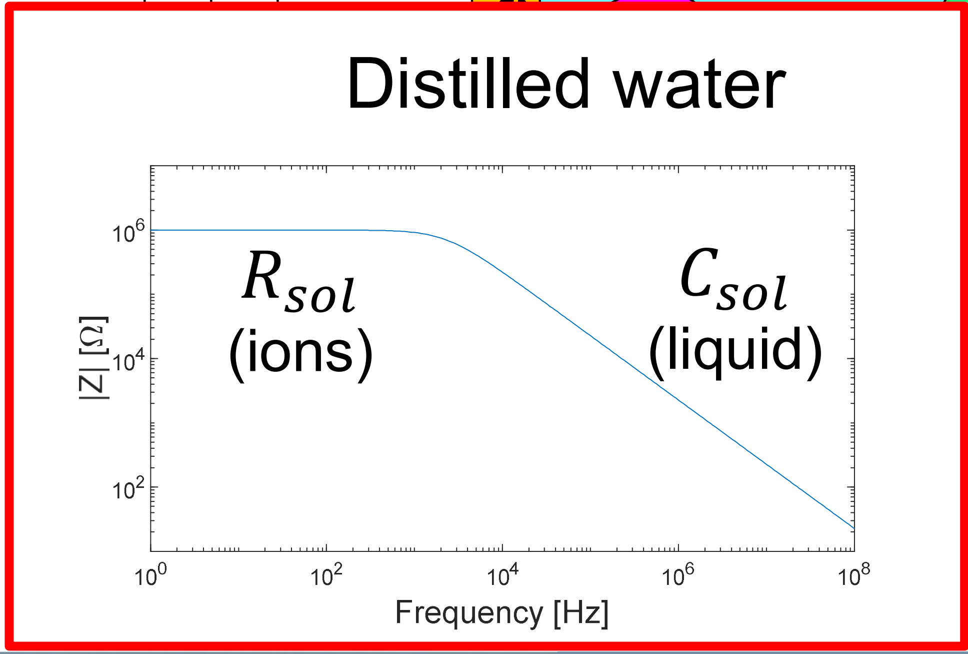
Conductive behavior

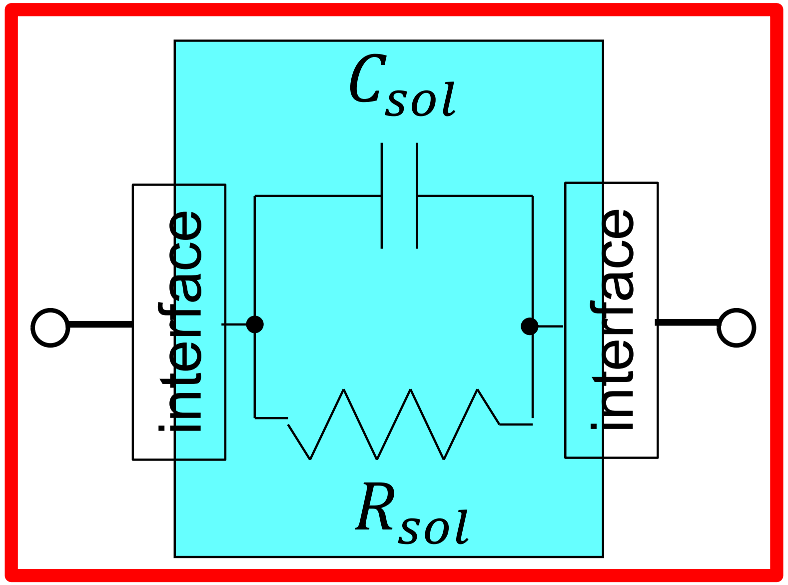
charge transport

Current given by induced charge + transferred charge









Charge Transport

- Diffusion

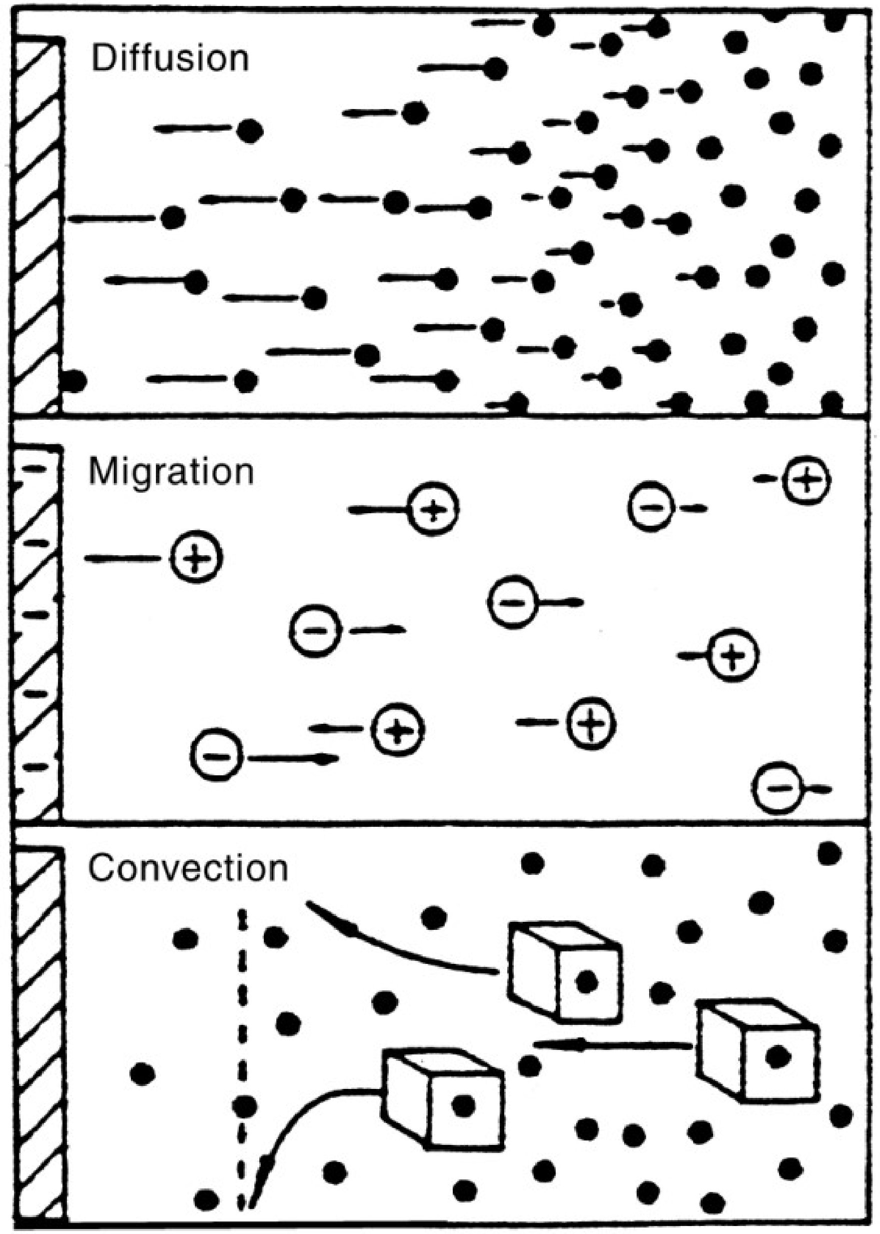
$$\propto \frac{\partial C_i(x)}{\partial x} \quad (C_i \text{ concentration})$$

- Drift (migration)

$$\propto C_i E(x) \quad (E \text{ electric field})$$

- Convection (fluid motion)
  - Natural (density gradient)
  - Mechanical (stirring, flow in microfluidic channel…)

$$\propto C_i v(x) \quad (v \text{ velocity of sol.})$$



Wang, Analytical Electrochemistry

Drift current

Current density due to the charged species i:

$$J_i = z_i q\, p_i \mu_i E(x)$$

z_i= number of charge (dimensionless) of species i

q= elementary charge (1.6 10^{-19} C)

μ_i = mobility [cm^2/Vs]

E(x) = electric field [V/cm]

p_i = concentration in #ions/cm^3 = $C_i \cdot N_{Av}$ /1000

N_{Av}=Avogadro const.
1 M → $6 \cdot 10^{23}$ ions/cm^3

C_i= ***molar concentration*** = mol / liter

$$J_i = z_i q \mu_i \frac{C_i N_{Av}}{1000} E(x)$$

$$I_{TOT} = \sum_i^{\text{all charged species}} A J_i$$

A= surface

F= Faraday constant = q N_{Av}

$$\sigma_i = z_i q\, p_i \mu_i = \frac{z_i F \mu_i C_i}{1000}$$

conductivity (1/resistivity)

Mobilities and diffusion coefficients

(low concentration, no interionic interactions)

Ionic mobilities of various ions in water [19]

Cation	Mobility (10^{-4} cm^2/Vs)	Anion	Mobility (10^{-4} cm^2/Vs)
H^+	36.3	OH^-	20.5
Li^+	4	F^-	5.7
Na^+	5.2	Cl^-	7.9
K^+	7.6	Br^-	8.1
NH_4^+	7.6	I^-	8.0
Ca^{2+}	6.2	NO_3^-	7.4
Mg^{2+}	5.5	HCO_3^-	4.6
La^{3+}	7.2	SO_4^{2-}	8.3
Ag^+	6.4	$Fe(CN)_6^{3-}$	10.5
$(CH_3)_4N^+$	4.7		

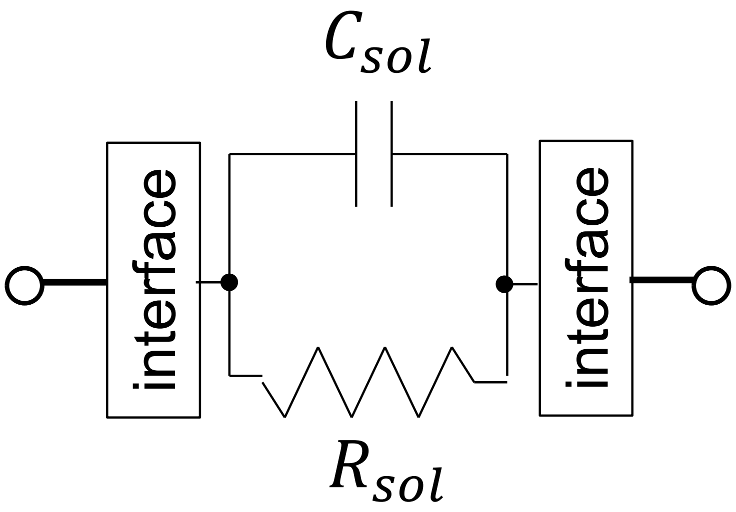
W. Shinwari ,Microelectronics Reliability 47 (2007) 2025–2057

$$\mu \approx 5 \cdot 10^{-4} \frac{cm^2}{Vs}$$

$$D \approx 10^{-5} \frac{cm^2}{s}$$

Silicon:
$\mu \approx 1000$ cm^2/Vs
$D \approx 20$ cm^2/s

Equivalent circuit of bulk solution

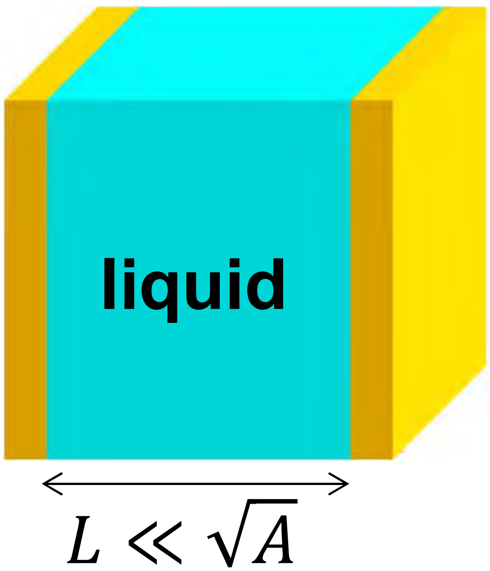


$$C_{sol} = \epsilon_{liquid}\, K_G$$ K_G is a geometrical factor

$$R_{sol} = \frac{\rho}{K_G} \propto \frac{1}{\mu \cdot Concentration}$$

C_{sol} and R_{sol} are *geometry-dependent*

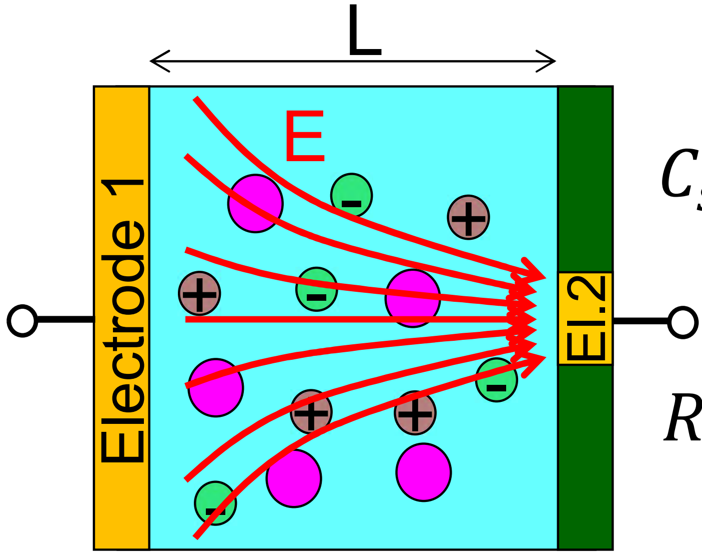
Parallel plate electrodes, area A



$$C_{sol} = \epsilon \frac{A}{L}$$

$$R_{sol} = \rho \frac{L}{A}$$

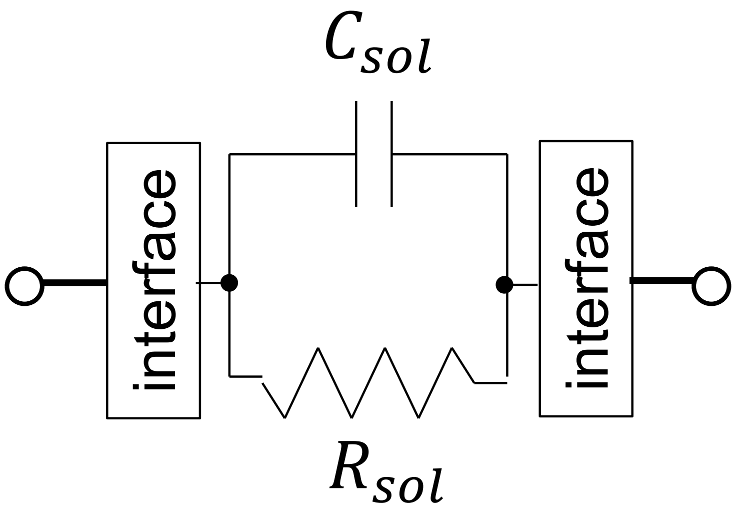
Small disk: diameter d ≪ L



$$C_{sol} = \epsilon\, 2d$$

$$R_{sol} = \rho \frac{1}{2d}$$

Dielectric relaxation time

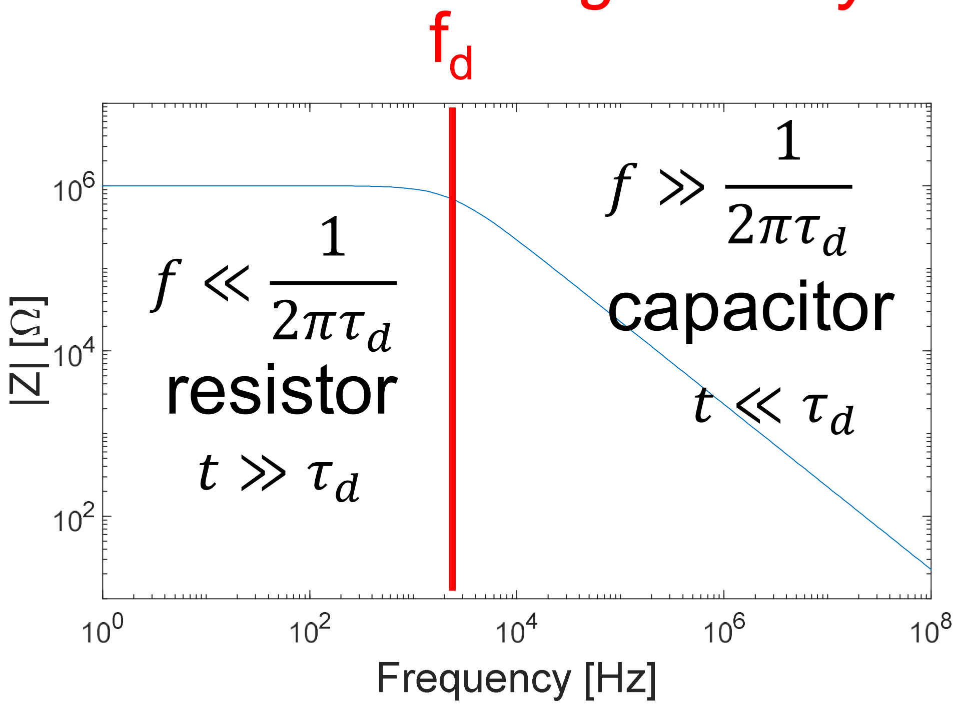


C_{sol} and R_{sol} are *geometry-dependent*

Dielectric relaxation time:

$$\tau_d = R_{sol} \cdot C_{sol} = \rho\epsilon \propto \frac{\epsilon}{\mu \text{ Concentration}}$$

geometry-independent



➡ bulk solution is a resistor up to $f_d \approx \frac{1}{2\pi\rho\epsilon} \propto \mu \cdot \text{Concetration}$

Examples of solution

- pure water:

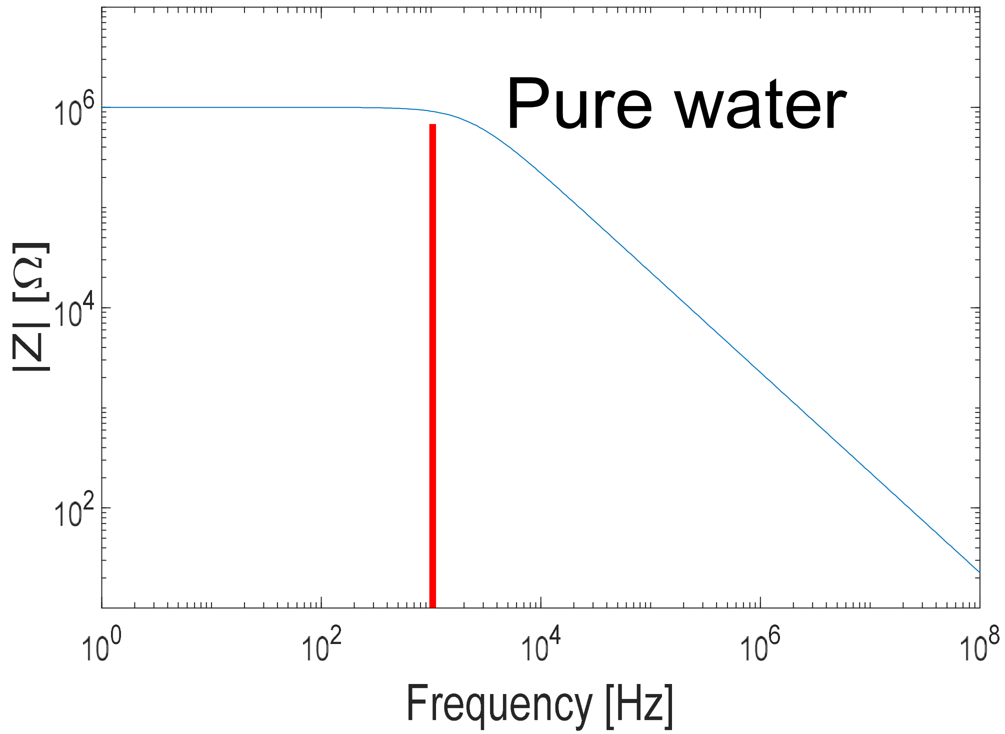
  pH = 7 → C_{H^+}= 10^{-7} M →

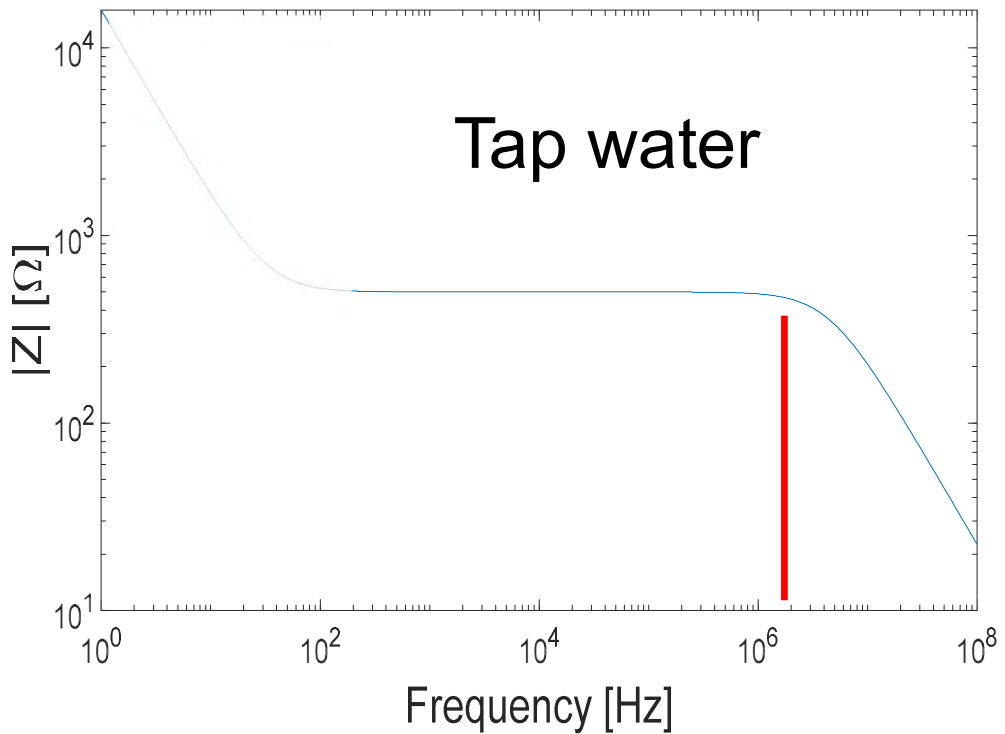
  ➡ $\tau_d \approx 140\mu s$, $f_d \approx 1$ kHz

- tap water:

  $\rho \approx 10$ kΩ· cm, $\varepsilon_r \approx 78$

  ➡ $\tau_d \approx 70ns$, $f_d \approx 2.3$ MHz





Examples of solution

- pure water:

  pH = 7 → C_{H^+} = 10^{-7} M → ρ ≈ 20 MΩ·cm, $\varepsilon_r \approx 78$

  ➡ $\tau_d \approx 140\mu s$, $f_d \approx 1$ kHz

- tap water:

  ρ ≈ 10 kΩ·cm, $\varepsilon_r \approx 78$

  ➡ $\tau_d \approx 70ns$, $f_d \approx 2.3$ MHz

- Phosphate Buffered Saline (PBS) commonly used for ***in-vitro biological research***

  Dulbecco's formula: 137mM NaCl; 8.10mM Na_2HPO_4; 2.68mM KCl;…

  1M means $N_A = 6 \cdot 10^{23}$ molecules per liter → ≈ 10^{20} ions/cm^3 !

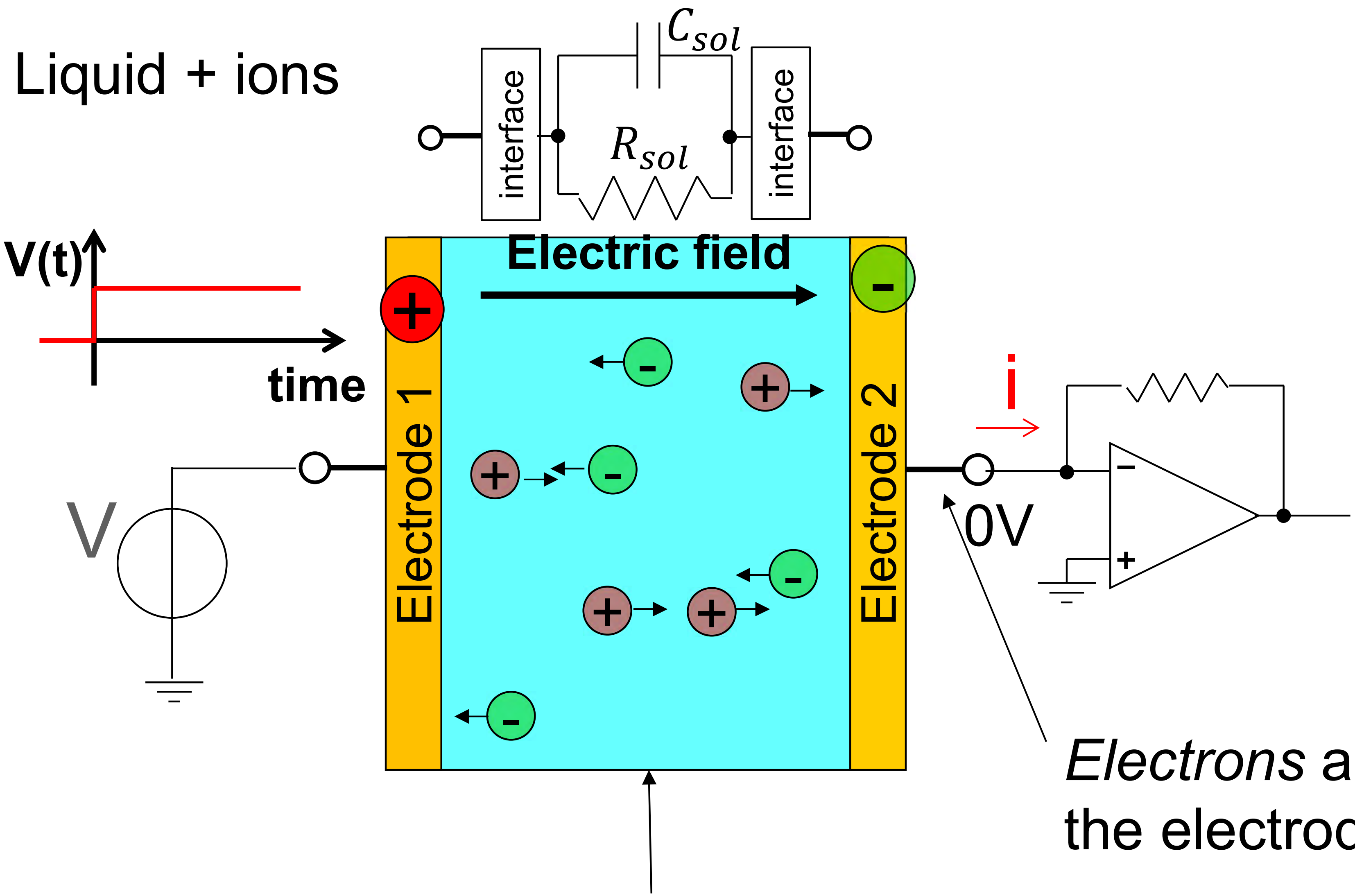
  ρ ≈ 60 Ω·cm, $\varepsilon_r \approx 78$

  ➡ $\tau_d \approx 0.5ns$, $f_d \approx$ 350 MHz

  same ρ of silicon doped with ≈10^{14} cm^{-3}
  moderate conductor for electronics

Electrical current in electrolytes

Liquid + ions



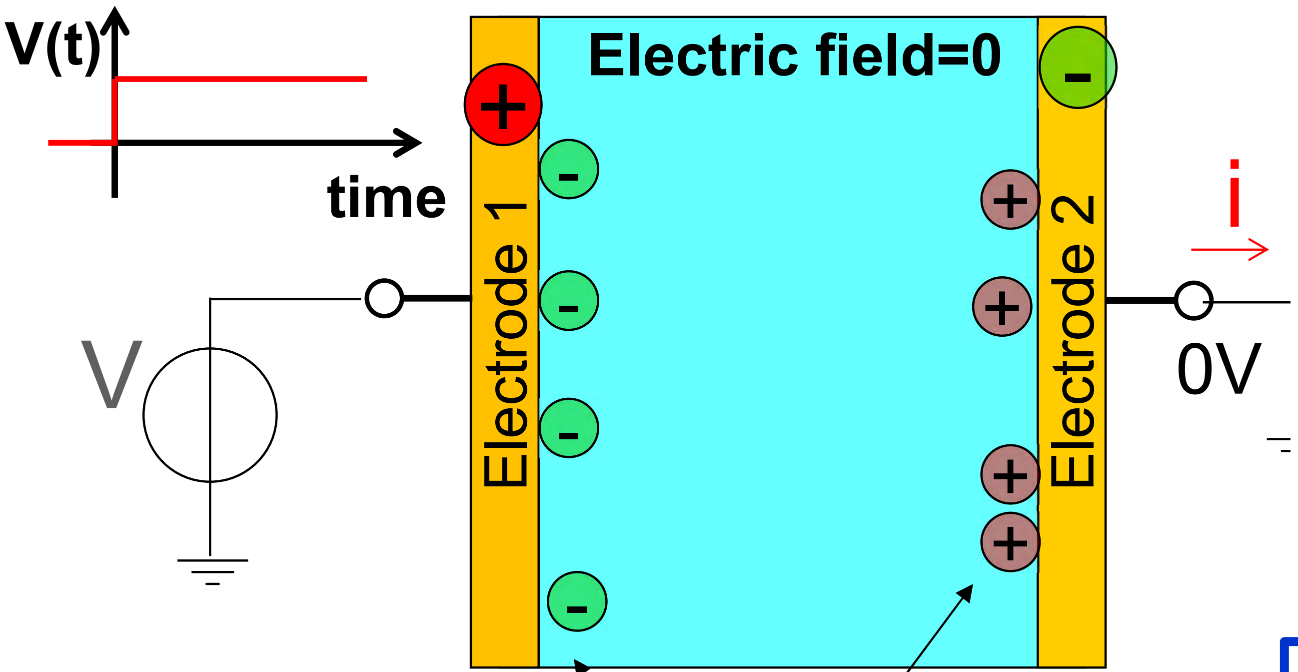
Electrons are moving in the electrodes

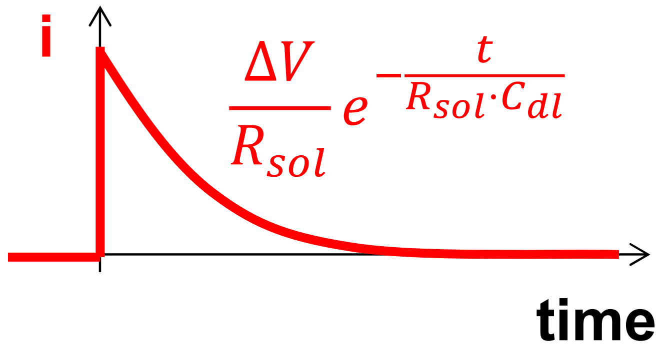
Ions are moving in the liquid

Electrical current in electrolytes

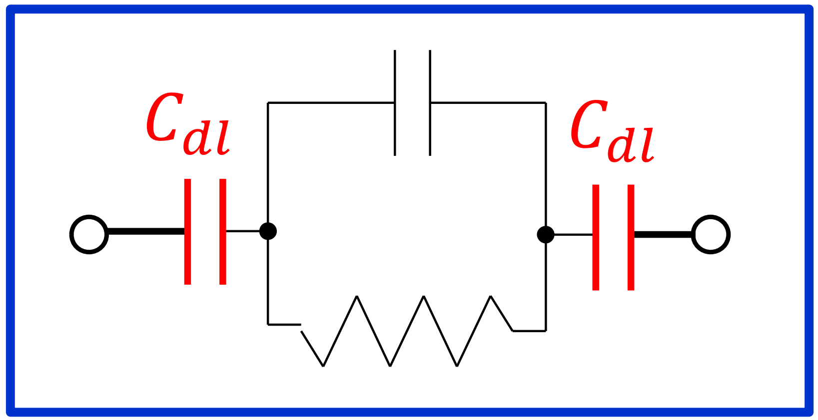
Liquid + ions

Accumulation of ions *in absence* of charge transfer at the interface



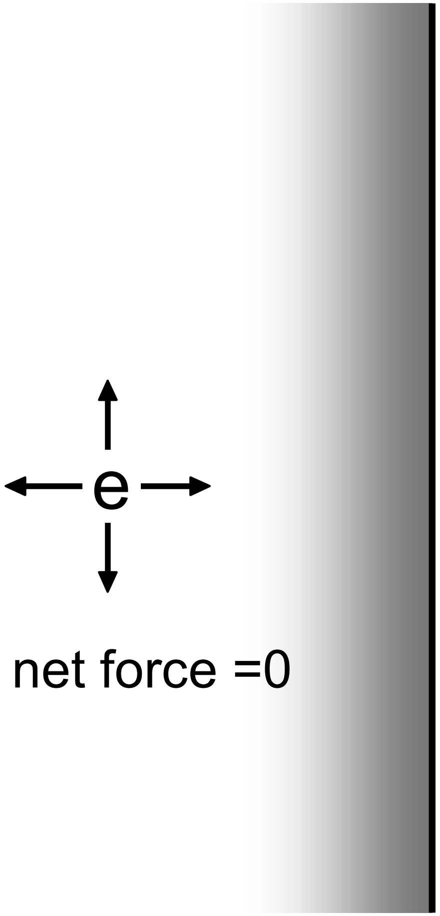


Ions shield the electrodes
→ no further charge transport



Metal-liquid interface

Metal



net force =0

Free electrons
in a crystal

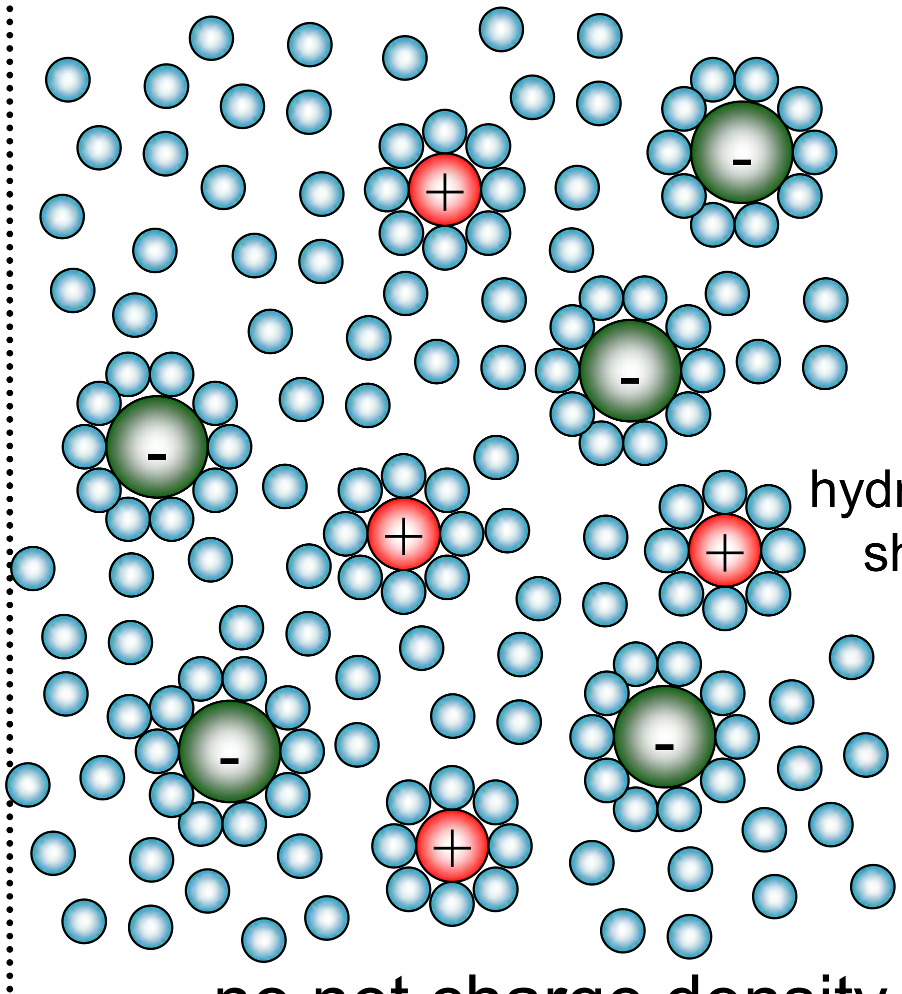
Interphase region

anisotropic
forces on
electrons, ions,
water molecules

Charge redistribution

Bulk Solution

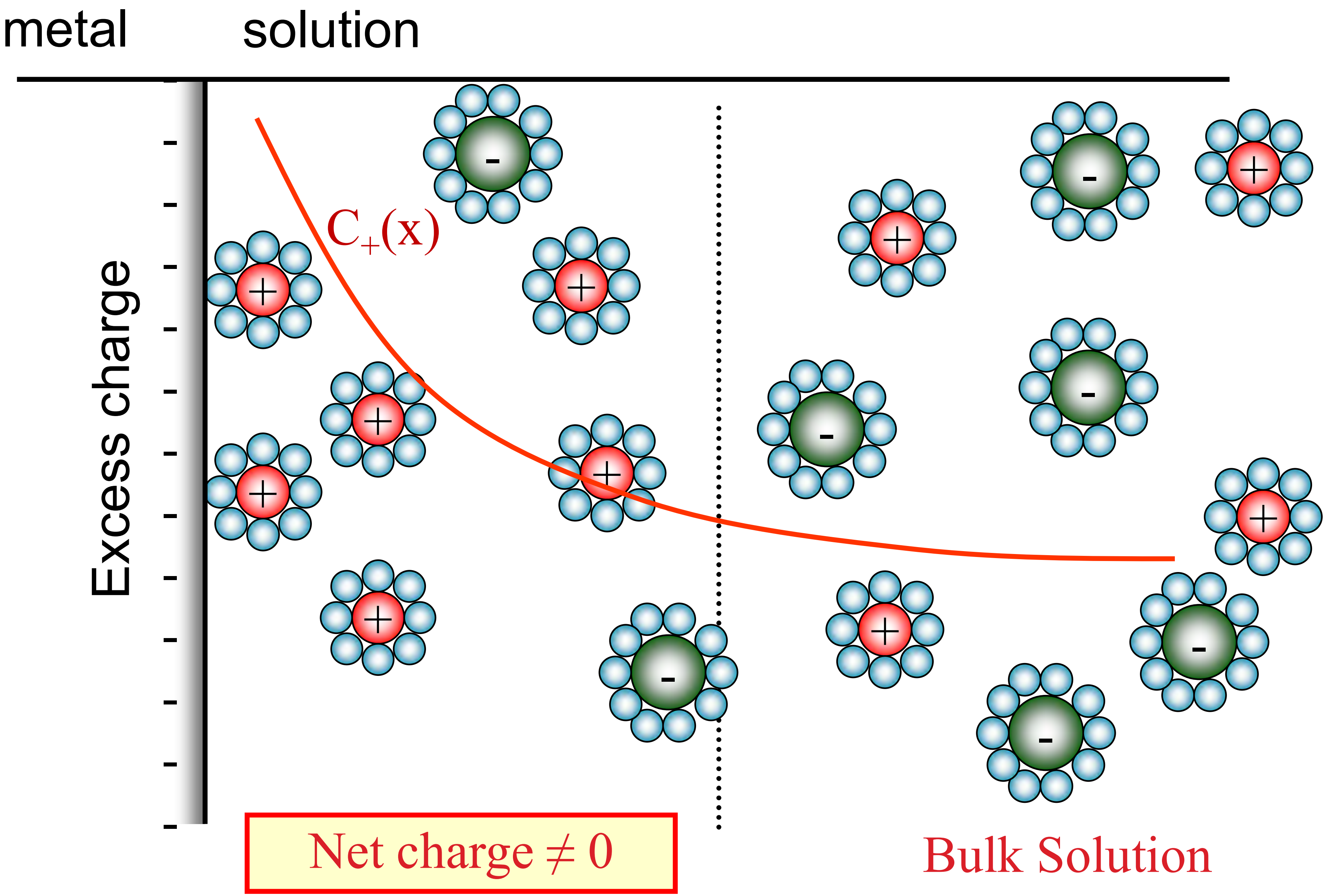
water molecule



hydration
shell

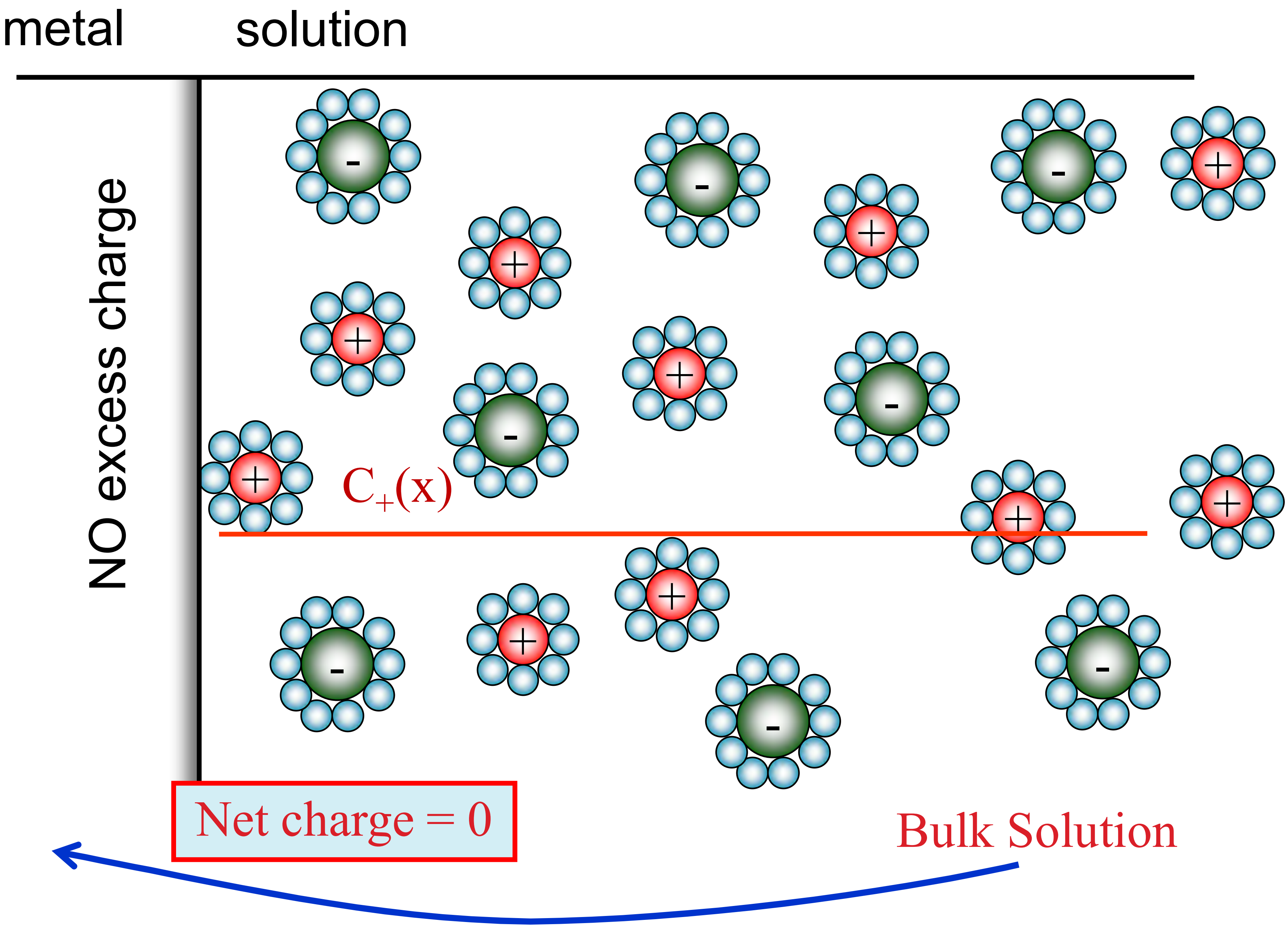
no net charge density
no net dipole orientation

Charge redistribution at the interface



The interface electric field can reach 10-100MV/cm!!!

Potential of zero charge

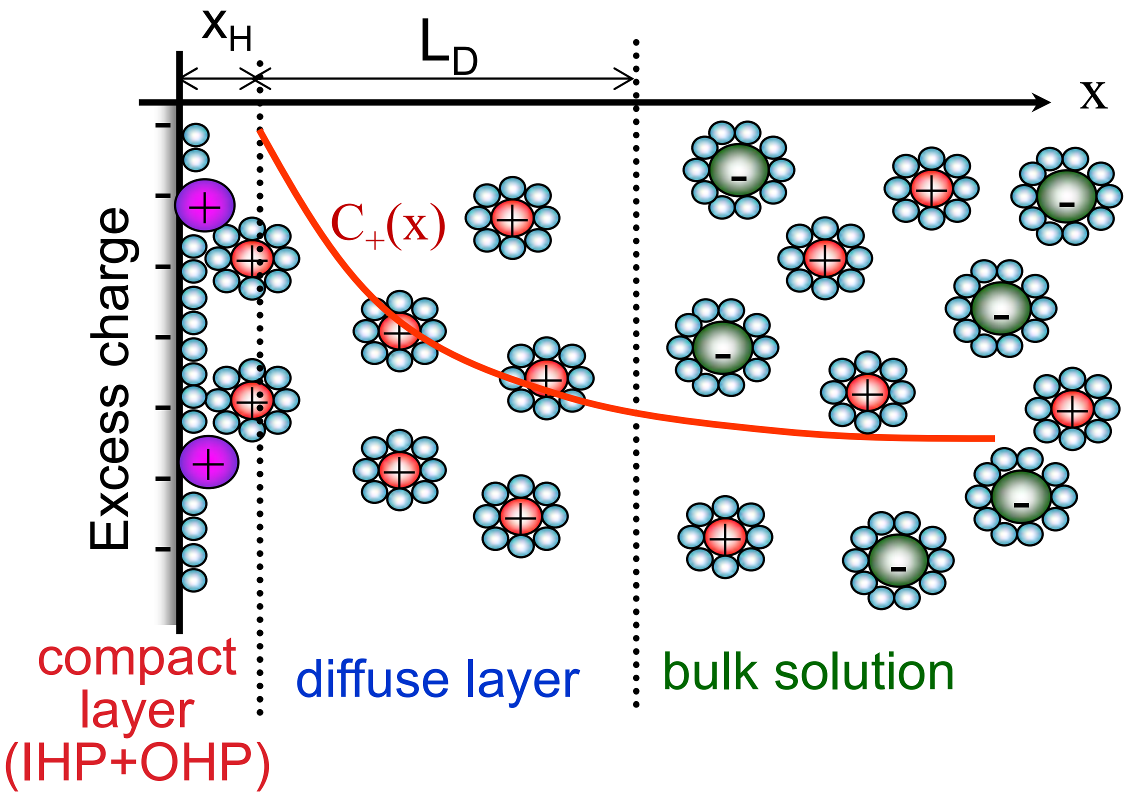


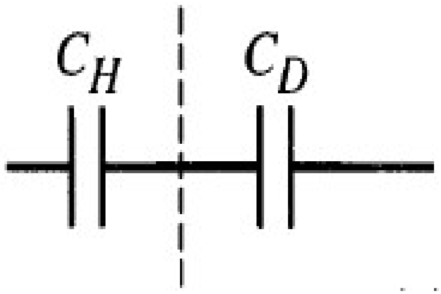
$\Delta V = V_{zero\text{-}charge}$

$Q_{acc} \approx C_{dl} (\Delta V - V_{zero\text{-}charge})$

Electrical Model (Stern model)

Restriction to the closest approach of ions





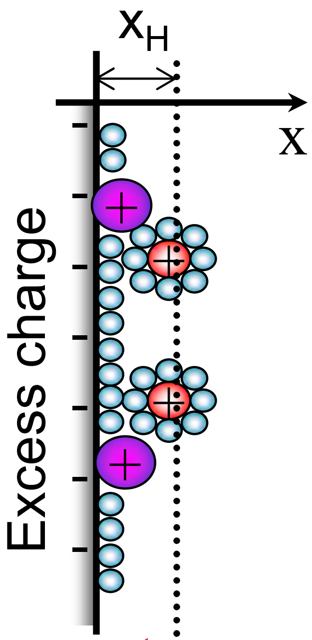
IHP (≈0.2nm): inner Helmholtz plane: specifically adsorbed ions (bond formation / desolvated)

OHP (≈0.4nm) outer Helmholtz plane: minimum distance of solvated ions (nonspecifically adsorbed, only electrostatic force)

Diffuse layer (≈1-10nm): distribution of ions from OHP to bulk due to thermal motion

Compact layer capacitance

Restriction to the closest approach of ions



compact layer (IHP+OHP)

What dielectric constant?

high electric field → water molecules oriented

↓

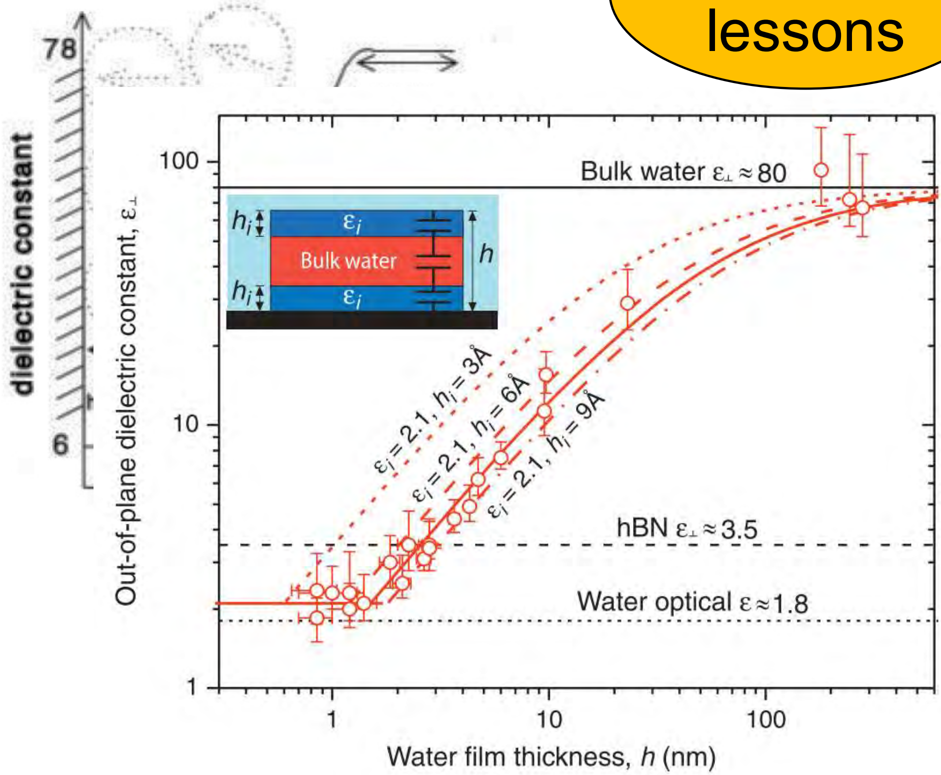
dielectric saturation

Fumagalli lessons

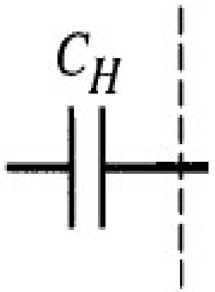
$\varepsilon_{H2O} = 78$

↓

$\varepsilon_{H2O,sat} \approx 6$



J.O.M. Bockris. Modern Electrochemistry



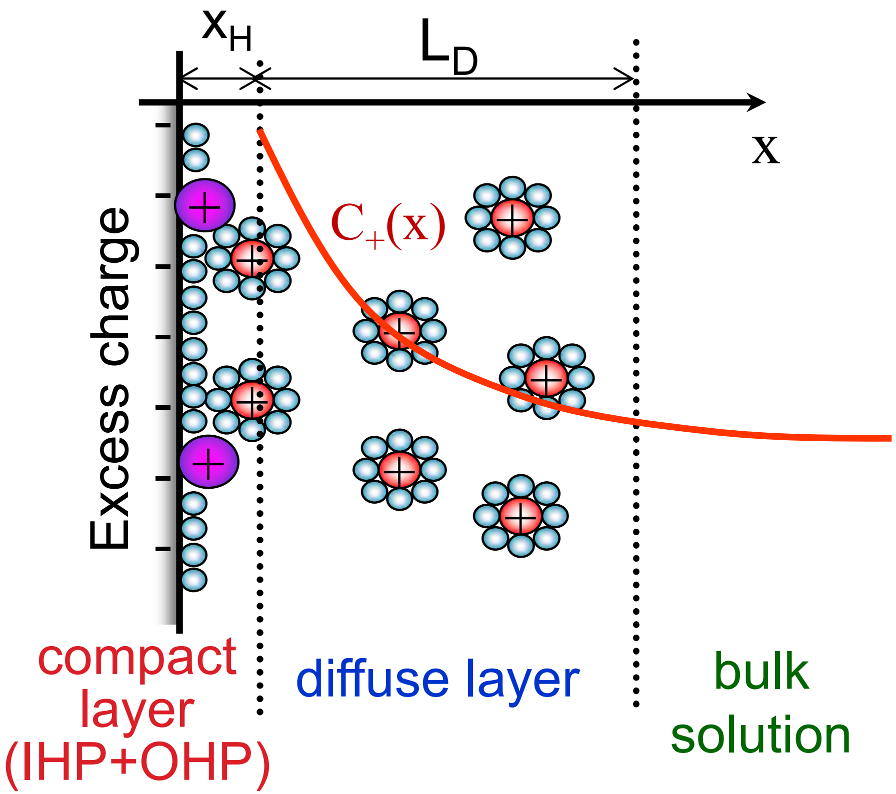
$$C_H = \epsilon \frac{A}{x_H}$$

(x_H<1nm!)

L. Fumagalli, et al. "Anomalously low dielectric constant of confined water," *Science*. 2018.

Diffuse layer capacitance

Ion concentration determined by Boltzman statistics + Poisson eq.



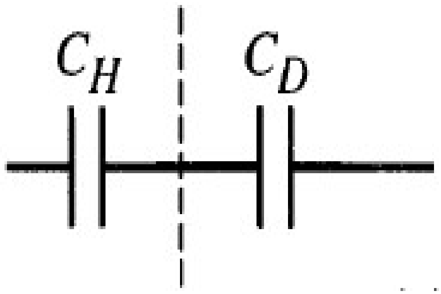
$$\frac{\tanh(zq\phi/4kT)}{\tanh(zq\phi_0/4kT)} = \exp\left(-\frac{x}{L_D}\right)$$

zq= charge of the single ion

ϕ_0= potential drop across the diffuse layer (V-$V_{zero\ charge}$)

for $\phi_0 < 50mV$:

$$\phi(x) \cong \phi_0 \exp(-x/L_D)$$



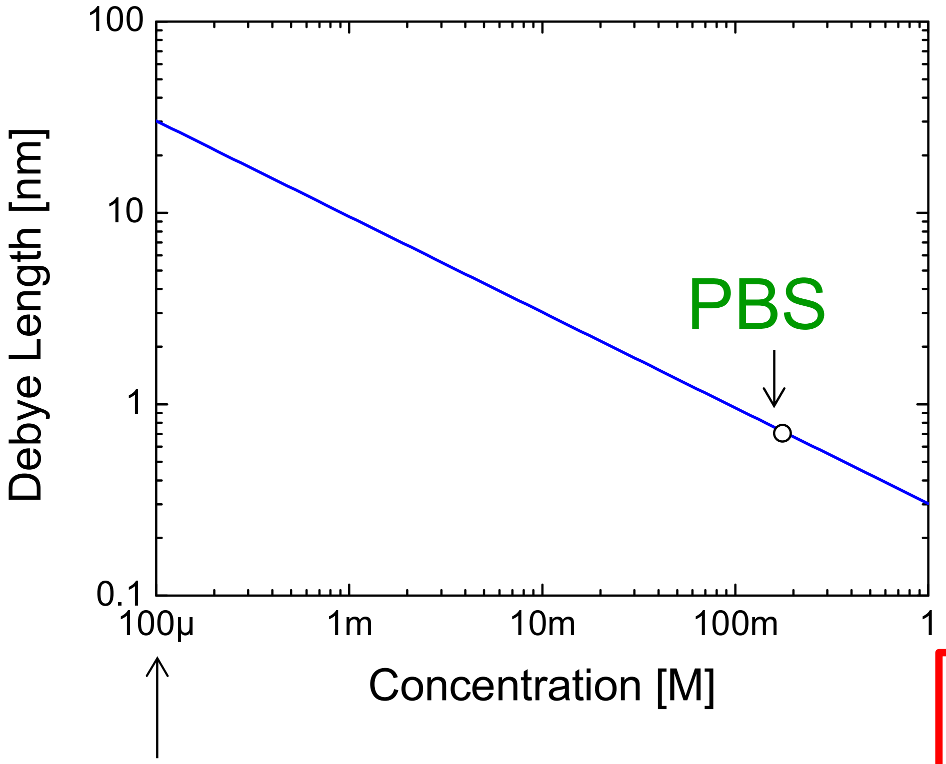
$$L_D = \sqrt{\frac{\epsilon kT}{2z^2q^2C_0}}$$

Debye length
diffuse layer "thickness"

C_0 = ion concentration in the bulk

Diffuse layer capacitance

Ion concentration determined by Boltzman statistics + Poisson eq.



6mg/liter of NaCl

pure water, pH=7 (100nM): $L_D \approx 1\mu m$

$$\frac{\tanh(zq\phi/4kT)}{\tanh(zq\phi_0/4kT)} = \exp\left(-\frac{x}{L_D}\right)$$

zq= charge of the single ion

ϕ_0= potential drop across the diffuse layer ($V-V_{zero\ charge}$)

for $\phi_0 < 50mV$:

$$\phi(x) \cong \phi_0 \exp(-x/L_D)$$

$$L_D = \sqrt{\frac{\epsilon kT}{2z^2q^2C_0}}$$

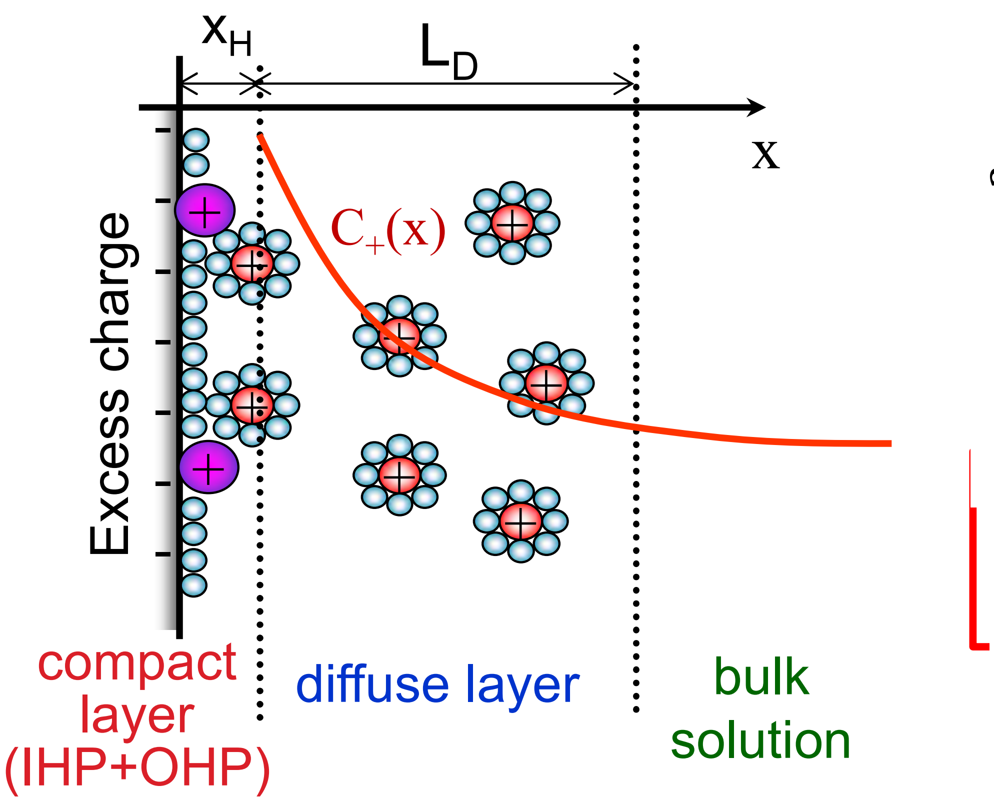
Debye length
diffuse layer "thickness"

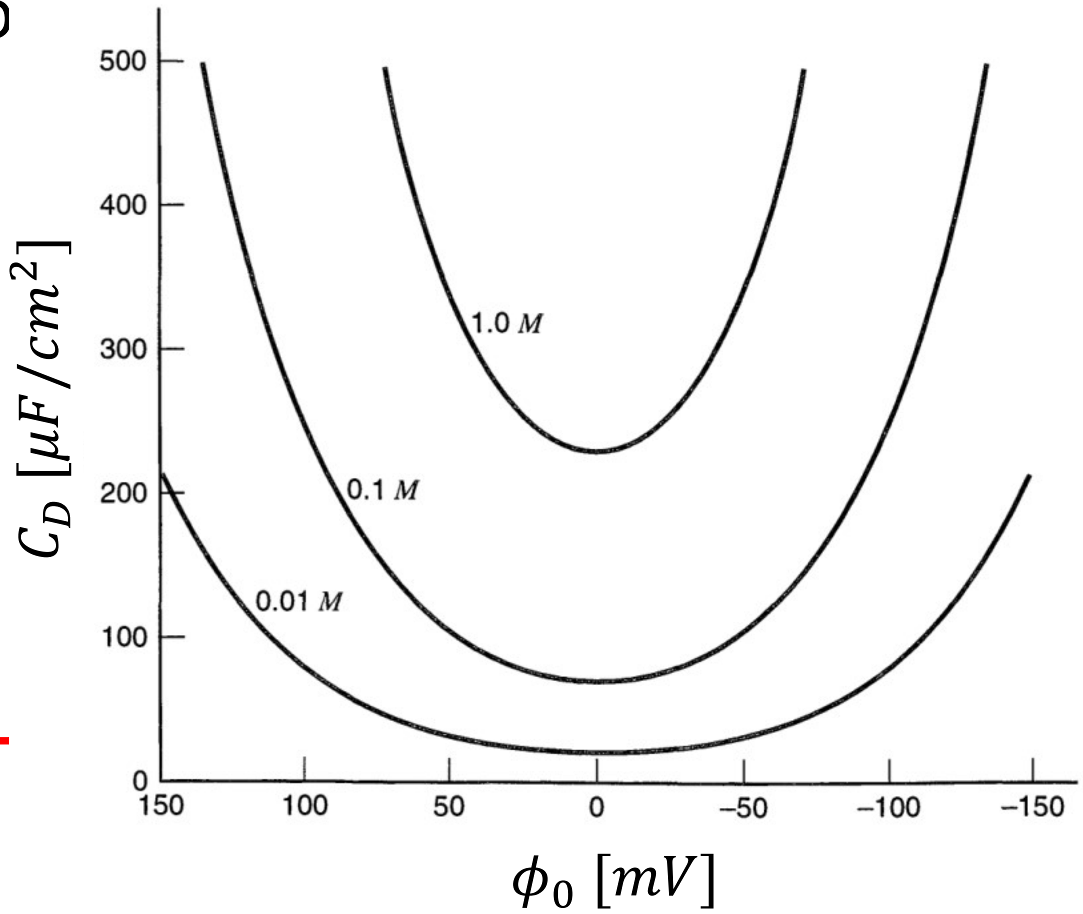
C_0 = ion concentration in the bulk

Note: any charge is screened by ions at a distance greater than ≈ L_D, keep this in mind when designing charge-based biosensors!

Diffuse layer capacitance

Ion concentration determined b





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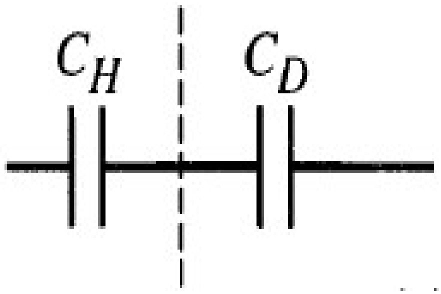
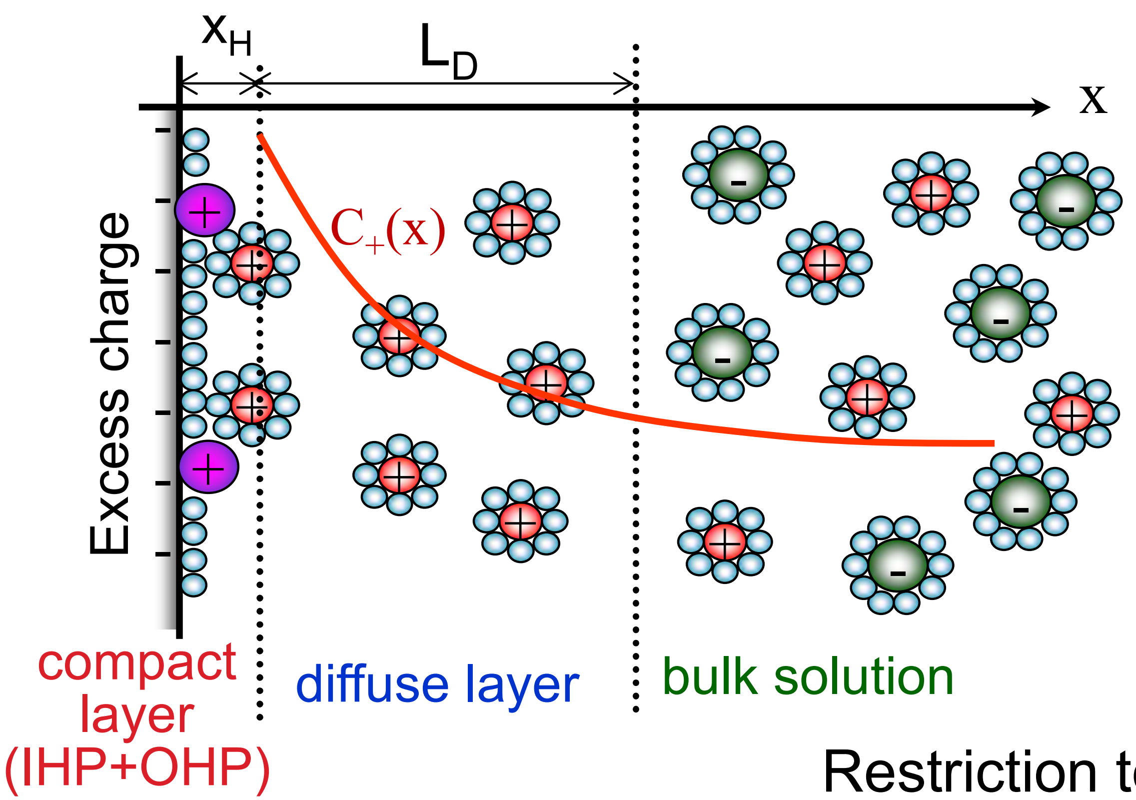


$$C_D = \frac{dQ}{d\phi_0} = \epsilon \frac{A}{L_D} \cosh\left(\frac{zq\Phi_0}{2kT}\right)$$

depends on the potential (Φ_0) and concentration (L_D)

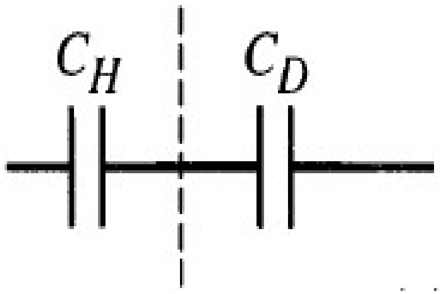
Electrical Model (Stern model)



Restriction to the closest approach of ions

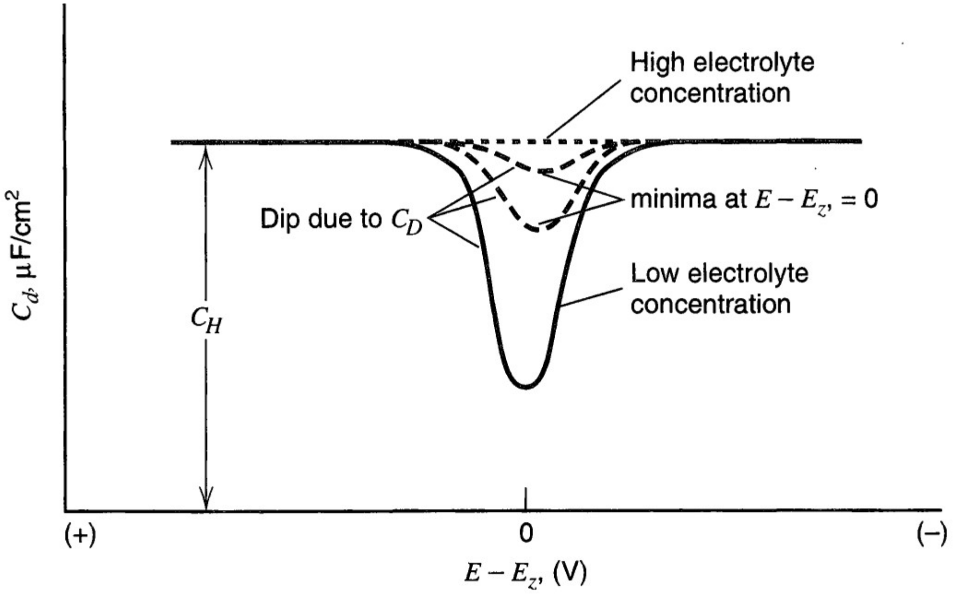
Variable charge density: diffuse layer

$$\frac{1}{C_{DL}} = \frac{x_H}{\epsilon_{sat}} + \frac{L_D}{\epsilon \cosh\left(\frac{zq\Phi_0}{2kT}\right)}$$



Double layer capacitance

Stern model



Bard, Faulkner, Electrochemical methods

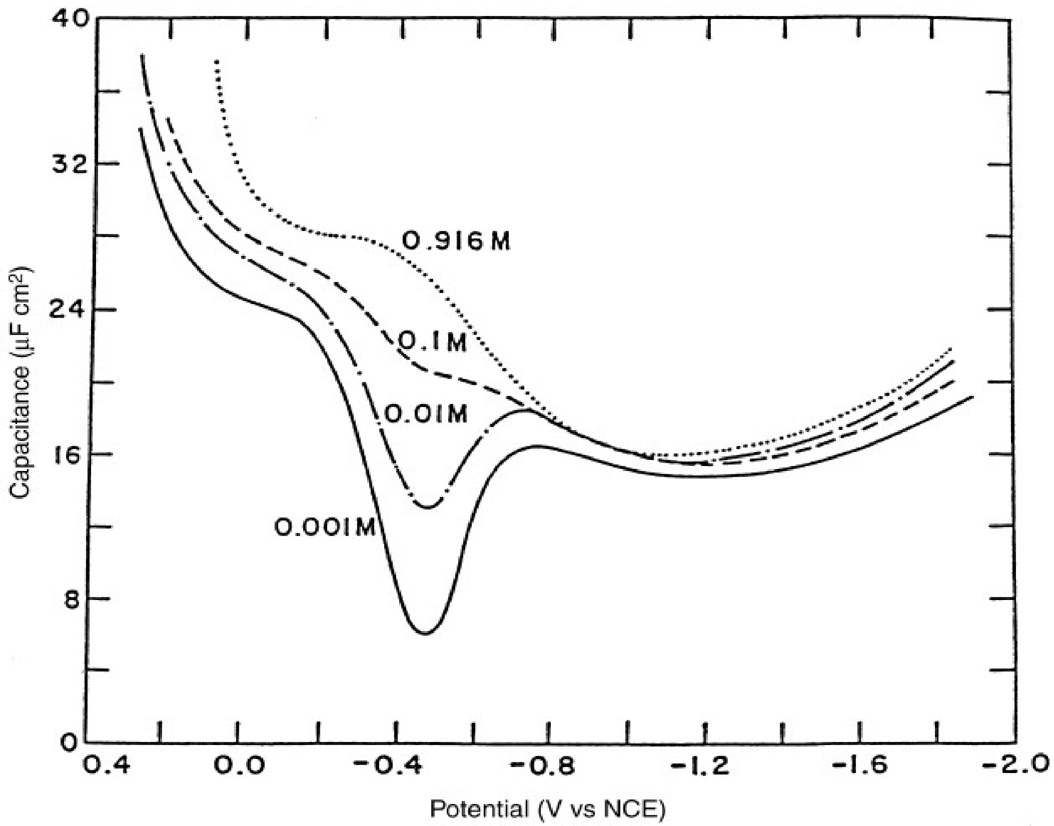


FIGURE 1-13 Double-layer capacitance of a mercury drop electrode in NaF solutions of different concentrations. (Reproduced with permission from reference 5.)

Wang, Analytical Electrochemistry

Minimum of C_{dl} at the potential of zero charge (PZC)

PBS:

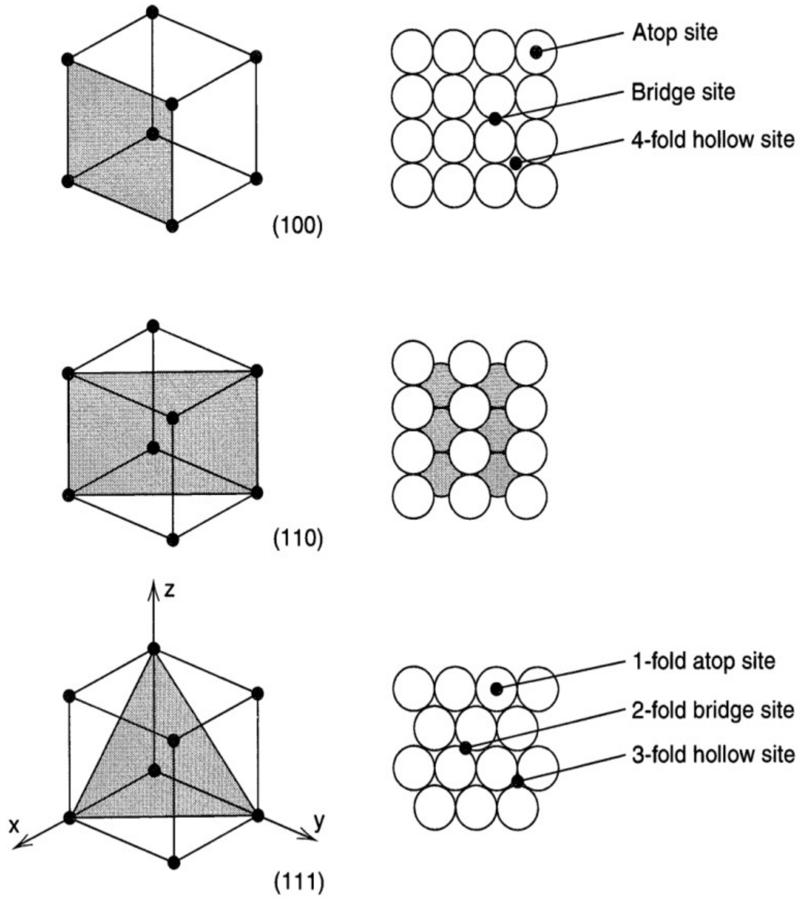
C_{dl}= 10 - 40μF/cm²
= 0.1- 0.4pF/μm²

C_H depends on potential, saturated dielectric, ion-ion interaction, adsorption,…

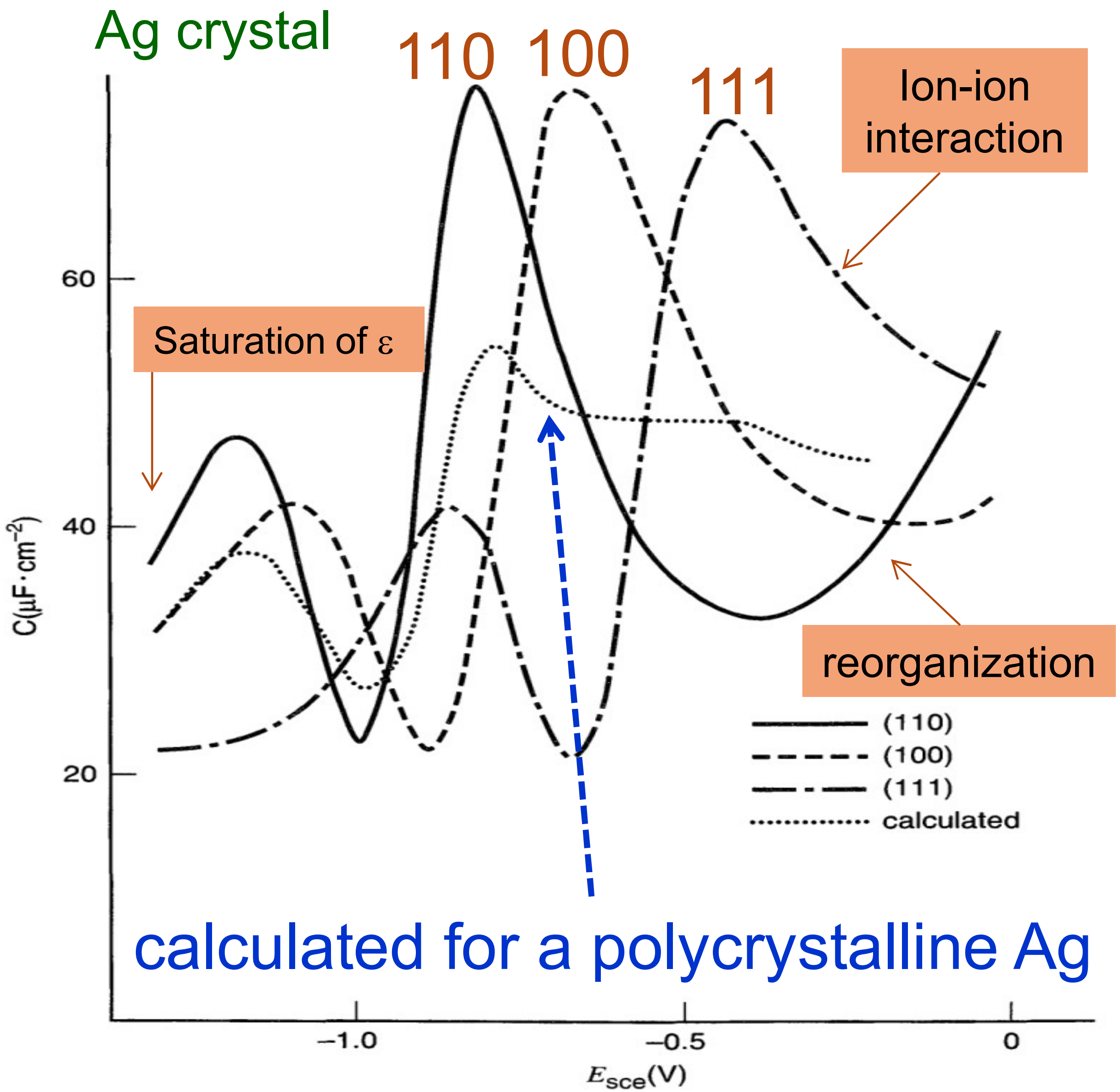
Strong sensitivity to the atomic structure of the surface !

Well-defined electrode surface

Strong sensitivity to the atomic structure of the surface!



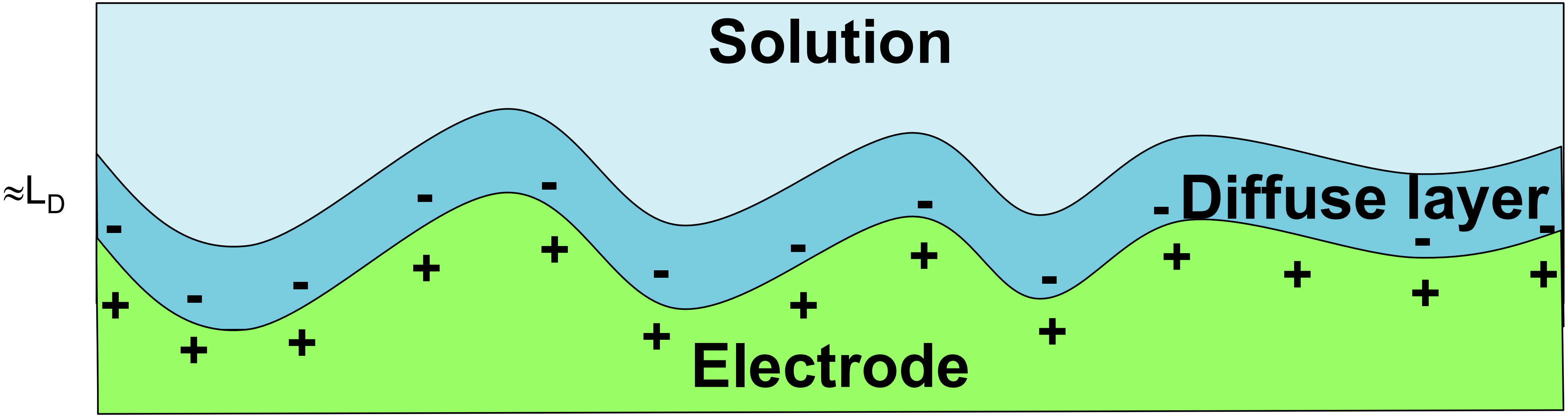
Face-centered cubic (FCC) structure



Bard, Faulkner, Electrochemical methods

«Real area» of an electrode

C_{dl} depends on the interfacial geometry on the L_D scale
(≈ 1nm in PBS!)



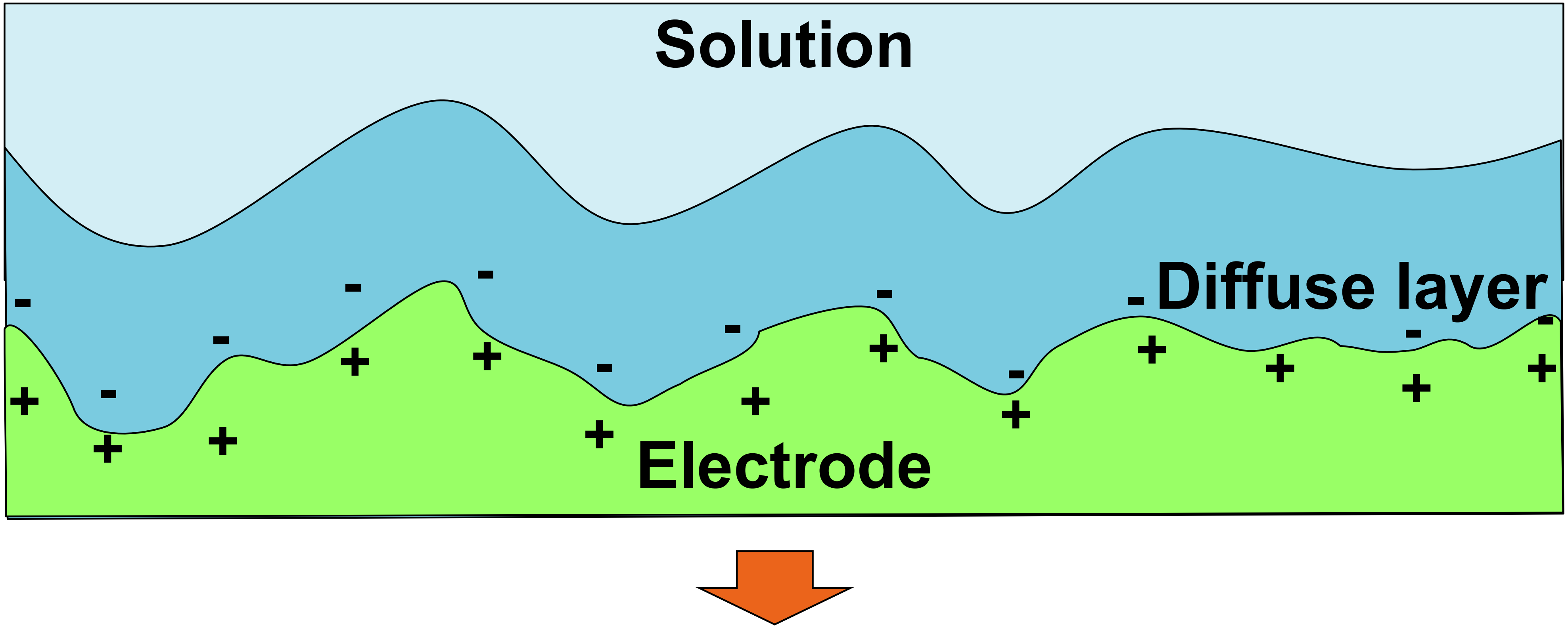
Double layer follows hills and valleys having size ≫ Debye length

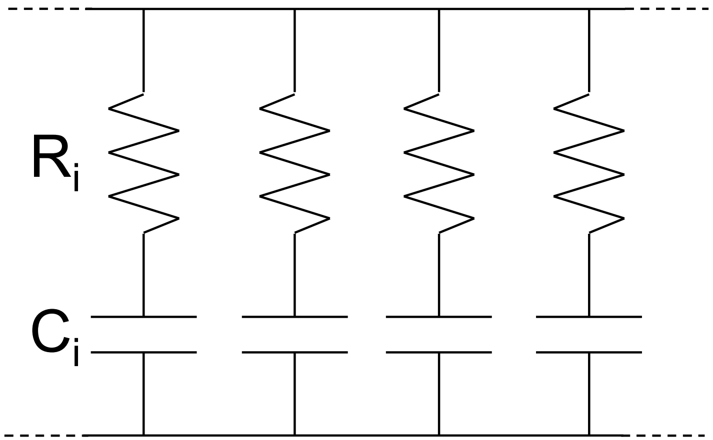
↓

The "microscopic area" of C_{dl} could be 2-3 times the macroscopic "geometrical area"

…and C_{dl} is affected by surface cleanliness: a 1 nm-thick layer of organic contaminants on the surface can halve the capacitance!

Atomic scale disorder

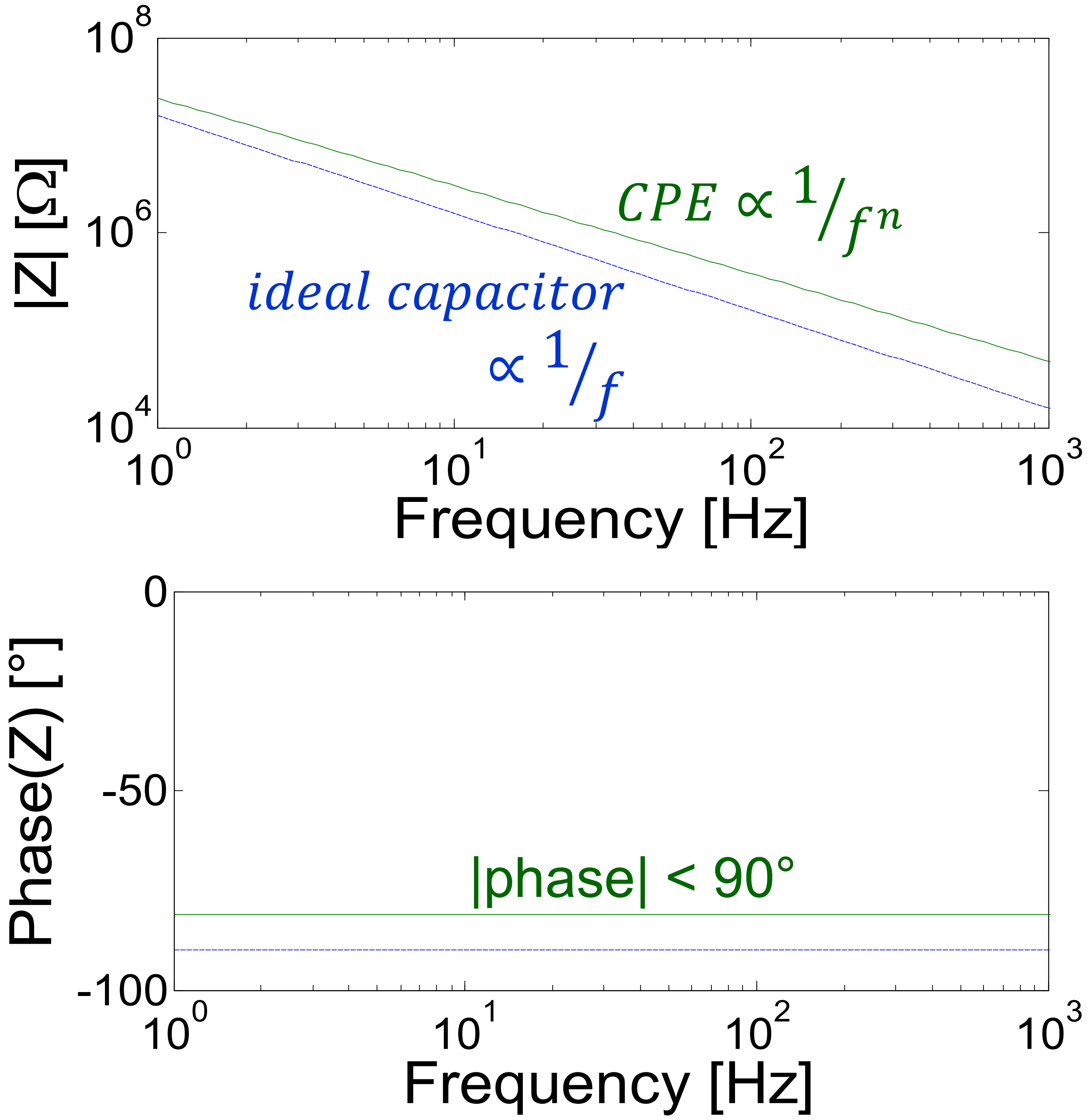




distribution of time constants

$$\frac{1}{Z} = Y = \sum_i \left(R_i + \frac{1}{sC_i} \right)^{-1}$$

Constant Phase Element



"Slope" of C_{dl} impedance is usually less than 1 (n = 0.8-0.9)

$$Z_{CPE} = \frac{1}{Q(j\omega)^n}$$

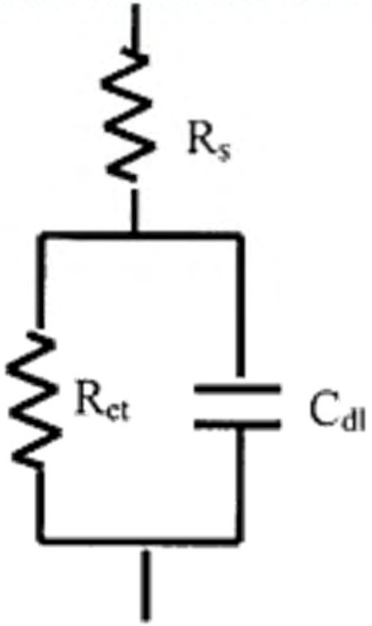
Excellent for fitting experimental data, but no clear physical insight, research is ongoing!

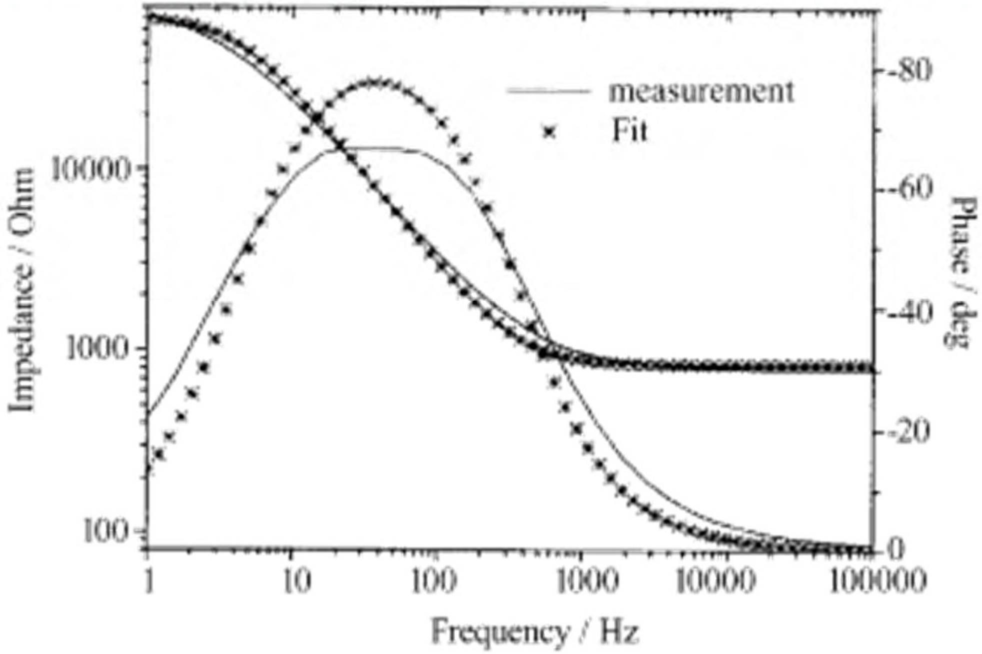
surface disorder, porous electrodes, adsorption, impurities,…

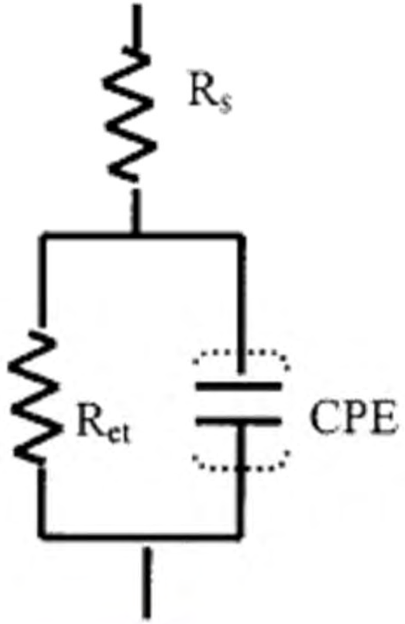
$$C_{eff} = Q^{1/n} R_{sol}^{(n-1)/n}$$

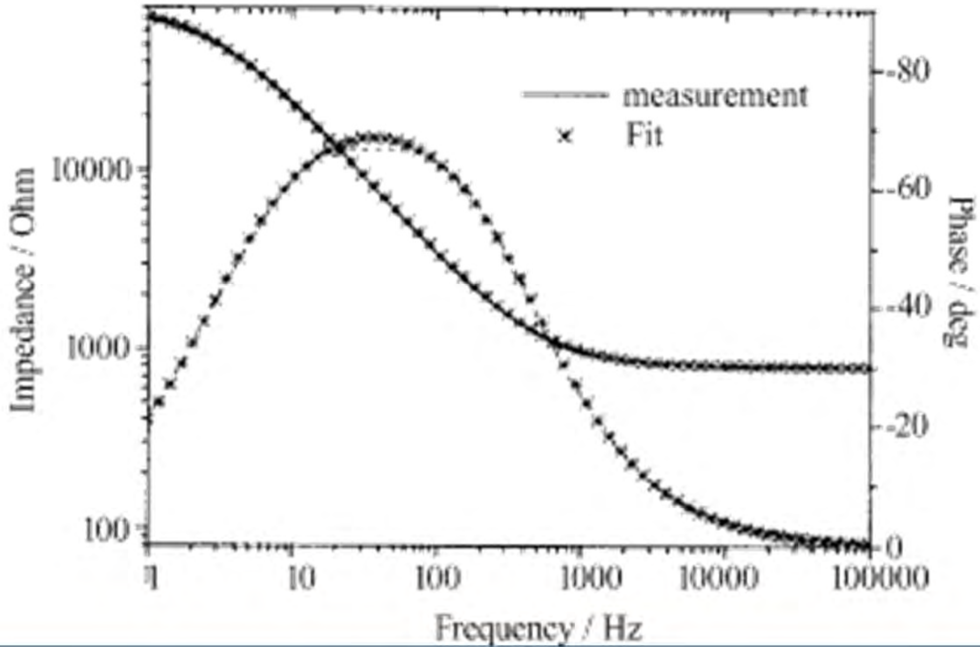
Lasia, *J. Phys. Chem. Lett.* 2022

CPE: Look at the Phase









Ding et al. / Electrochimica Acta 50 (2005) 3660–3666

Summary

- Ions make the liquid a conductor: very small mobility (≈ $5 \cdot 10^{-4}$ cm^2/Vs), but the ion concentration could be high (PBS: ≈10^{20} $ions/cm^3$)
- $R_{solution}=\rho \cdot$ geometrical factor, $C_{solution}= \varepsilon$ / geom. factor

$$1/\rho = \sum z_i q\, p_i \mu_i = \sum z_i q \frac{N_{av} C_i}{1000} \mu_i, \quad \varepsilon=78 \text{ (water)}$$

- Resistive behavior up to frequency ≈ $1/(2\pi\rho\epsilon)$
  physiological solution (PBS) is a "reasonable" conductor up to ≈350MHz
- Metal-liquid interface: a complex charge redistribution
  → double-layer capacitance
- C_{dl} has an enormous value (PBS: 10-40μF/cm^2) since the Debye length is usually in the nm scale
- Double layer is sensitive to the roughness and atomic structure of the surface → C_{dl} is not a very well-controlled value
- In many practical cases, C_{dl} is an imperfect capacitor
  → constant phase element: $Z_{CPE} = \frac{1}{Q(j\omega)^n}$

Small signal equivalent model